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Challenges and Opportunities in Synthesizing High Volume Chemicals from CO₂ without Direct H₂ Input

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Abstract: Decarbonizing the chemical industry will eventually entail using CO₂ as a feedstock for chemical synthesis. However, many chemical syntheses involve CO₂ reduction using inputs such as renewable hydrogen. In this review, we discuss chemical processes that use CO₂ as an oxidant for upgrading hydrocarbon feedstocks. The captured CO₂ is inherently reduced by the hydrocarbon co-reactants without consuming molecular hydrogen or renewable electricity. This CO₂ utilization approach can be potentially applied to synthesize 8 emission-intensive molecules, including olefins and epoxides. We discuss catalytic systems and reactor concepts that can overcome practical challenges, e.g. thermodynamic limitations, over-oxidation, coking and heat management. Under the best-case

combined CO₂ abatement potential of ca. 1 gigatons per year and avoid the consumption of 1.24 PWh renewable electricity, based on current market demand and supply.

1. Introduction

In 2015, 81% of our energy consumption was derived from fossil-based raw materials (coal, oil, and natural gas) with renewables and nuclear accounting for the remaining 19%.^[1] Increasing fossil fuel consumption and unrestricted greenhouse gas emissions (GHG, primarily CO₂) have led us significantly off-track from the pathway to mitigate climate change. To curb CO₂ emissions whilst meeting the increasing energy demand, the balance between fossil-based and renewably sourced raw materials must undergo a paradigm shift. As illustrated in Figure 1, we envisage a future scenario where captured CO₂, biomass, and recycled waste emerge as sustainable raw materials for manufacturing chemicals and fuels. Introducing these newer age feedstocks into the chemical supply chain will mandate the use of markedly different chemical processes, including new catalysts, new reactors, and new separation technologies.

Among the sustainable raw materials, the conversion of captured CO₂ is particularly important for developing a carbon circular economy via the carbon capture and utilization scheme (CCU).^[2–6] In particular, CCU offers a plausible decarbonization solution for regions with limited CO₂ sequestering potentials. Today, the chemical industry already consumes CO₂ as a raw material for the production of important chemicals, such as salicylic acid, urea, polycarbonates, sodium bicarbonate, etc.^[7] Most of these commercial CO₂-to-chemical conversions are energetically downhill and do not involve change in the oxidation state of carbon. In fact, the production of carbonates and carbamates from CO₂ represents the “low-hanging fruit” for implementing CCU.^[8] On the other hand, the demand for CO₂ by existing industrial processes is only 0.3% of the total amount emitted.^[2] Therefore, building a carbon circular economy requires us to substantially broaden the pool of chemical syntheses that utilize CO₂. Ideally, this pool should encompass chemicals with the highest energy intensities and the largest CO₂ footprints. Recent successes in developing new CO₂ utilization processes have been evident through pilot scale demonstrations of the production of C₁ (CO, CH₄, CH₃OH) and C₂ (oxalic acid) chemicals from CO₂.^[2] Meanwhile, the syntheses of multi-carbon products, e.g. higher olefins, oxygenates, and aromatic compounds remain at low technological readiness levels (TRL), owing to difficulties in controlling product selectivity and minimizing catalyst deactivation, e.g. by coking. The interested reader is directed to the following reviews and perspectives that discuss thermal,^[9] electro-,^[10] photo-,^[11] and plasma-catalysis^[12] approaches for synthesizing C₁ building blocks (e.g. CO,^[10] CH₄,^[13] and CH₃OH),^[9] higher alcohols,^[14] higher olefins,^[15] and fuels^[16] from CO₂. Several reviews highlight the active site speciation of catalysts,^[9] design principles for engineering selective active sites,^[14] and reaction

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scenario, these hydrogen-free CO₂ reduction processes have a

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mechanisms of CO₂ reduction pathways.^[9] Recent reviews by Otto et al.^[3] and Burkart et al.^[2] discuss the broad palette of chemicals that can be potentially synthesized from CO₂.

In contrast with synthesizing carbonates and carbamates, reactions in the broadened CO₂-to-chemical scheme often involve reduction of CO₂, e.g. by CO₂ hydrogenation.^[3] For the overall process to be carbon neutral or even carbon negative, the H₂ must be produced from renewable sources, e.g. water electrolysis by renewable electricity. Today, only 0.1% of H₂ consumed is produced from renewables, primarily owing to the prohibitively high cost: 'green H₂' (produced by electrolysis using renewable electricity, at \$6 per kg) is much more expensive than 'grey H₂' (produced from fossil fuels without carbon capture, at \$1.6 per kg).^[17] Indeed, a planetary boundaries analysis by Gonzalez-Garay et al. showed that the high cost of renewable H₂ is the principal factor making methanol production from CO₂

economically unattractive.^[18] Tackett et al. argued that the efficiency of state-of-the-art water electrolyzers must increase by orders of magnitude before CO₂ reduction by renewable hydrogen becomes commercially viable.^[19] Additionally, the scale at which the captured CO₂ needs to be reductively converted translates to an unrealistically high demand for renewable electricity.^[6] Therefore, scalable solutions that transform CO₂ to chemical products without direct H₂ inputs are highly desirable.^[20] Amongst the 18 most produced chemicals, which contribute to 63% of energy consumption and 75% of GHG emissions of the global petrochemical industry,^[21] eight of them can be potentially synthesized from captured CO₂ without direct H₂ input. With current industrial practices, the production of these 8 bulk chemicals, as quantitatively illustrated in Figure 2, corresponds to 35% of energy used and 34% of the GHG emitted by the petrochemical industry in 2010.^[21]

Figure 1. (a) Per capita energy consumption in 2015 was estimated to be ~2.5 kW (world population, 7.34 billion). (b) Per capita energy consumption in 2070 is forecasted to be ~3.4 kW (world population in 2070, 9.4 billion). The grand challenge of supplying this additional energy without increasing greenhouse gas (GHG) emissions will only be possible by introducing newer age feedstock like captured CO₂, biomass, and recycled waste.

Figure 2. (a) Energy consumption and production volumes of 8 large volume chemicals. (b) Global GHG emissions (Mt-CO₂ equivalent) for these chemicals. Taken together, these 8 large volume chemicals emit 5.4 exajoules of energy (36% of energy consumption from the (petro)chemical sector) and emit 434 Mt-CO₂ equivalent (35% of emissions from the (petro)chemical sector). Data adapted from Ref. [20]

In the scheme outlined in Figure 3, bio-syngas is produced by dry reforming of biomass-derived methane, ethanol, glycerol, and pyrolysis oil. Methane can be obtained from the anaerobic digestion of organic waste. Fermentation of biomass or organic waste produces bio-ethanol. Glycerol is a co-product of bio-diesel production, whereas bio-oil is produced from the pyrolysis of biomass and biowaste. After upgrading (e.g. by water-gas-shift

reaction), the bio-syngas can be used to synthesize green methanol, olefins, or liquid fuels. Furthermore, the methane obtained from biogas can react with CO₂ to produce C₂₊ hydrocarbons through the oxidative coupling reaction (OCM). The process simultaneously generates CO and H₂O for further chemical synthesis. Light alkanes that are synthesized either by OCM or extracted from shale gas can be dehydrogenated using

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CO₂ as a soft oxidant (CO₂-ODH) to form olefins and CO. The ethylene and propylene produced by CO₂-ODH can be either polymerized to polyethylene and polypropylene or oxidized to ethylene oxide and propylene oxide, respectively. The styrene produced by CO₂-ODH of ethylbenzene is a key building block for the manufacturing of synthetic rubber. Ethylene and propylene oxides are combined with CO₂ to synthesize cyclic carbonates and polycarbonates. These CO₂ utilizing reactions are already widely deployed in the chemical industry today. Crucially, none of the processes highlighted in Figure 3 involves direct H₂ input, thereby alleviating a critical techno-economic bottleneck. In the context of the proposed scheme, the captured CO₂ serves two functions: (i) reducing the GHG footprint by creating carbon-circular production routes and (ii) functioning as a soft oxidant. This review is organized according to the following sections. In section 2, we provide an overview of the processes shown in Figure 3, and discuss the thermodynamics of different classes of CO₂ reduction reactions, viz. (i) dry reforming of bio-feedstocks, (ii) oxidative dehydrogenation of alkenes by CO₂, (iii) oxidative

coupling of methane using CO₂, (iv) alkene epoxidation and its subsequent conversions using CO₂ and (v) direct CO₂ coupling to CH₄ to make carbonyls. In section 3, we review the development of catalysts for the reactions classified above, with a special emphasis on catalyst design principles to mitigate coking and suppress undesired side reactions such as C-C scission. Besides the need for catalysts with high activity, selectivity and durability, the high energy demand associated with separating multiple gas phase products (e.g. alkanes, alkenes, CO₂ and CO) must also be addressed. Section 4 illustrates how reaction engineering approaches can possibly (i) circumvent certain thermodynamic limitations and (ii) achieve product separation with low parasitic energy penalty. Since this paper focuses on H₂-free CO₂ utilization and collectively discusses reaction thermodynamics, catalyst requirements, and reaction engineering, it is complementary to existing reviews which are largely themed on engineering catalysts for H₂-based CO₂ utilization and high-level CCU pathway analysis.^[2,3,22,23]

Figure 3. Synergistically combining captured CO₂, with biomass, waste, and existing hydrocarbon resources to produce 8 large volume chemicals (purple font). All processes discussed here employ captured CO₂ as a raw material. Crucially, in these processes CO₂ is reduced without any direct addition of hydrogen. Using CO₂ as a feedstock and avoiding green hydrogen substantially contribute to decreasing the GHG footprint for manufacturing these large volume chemicals. CO produced from CO₂ reduction is shown in brown while flow streams for H₂O are not shown.

2. Process description and thermodynamics

2.1. Dry reforming of biofuel

Most commonly, the oxidation of hydrocarbon feedstocks by CO₂ yields syngas via CO₂ reforming, also known as dry reforming. When renewable hydrocarbon feedstocks (e.g. biomass and biofuels) are used, dry reforming can be considered a net CO₂ negative process.^[24] Here, we discuss the dry reforming of three

highly representative bio-derived molecules, viz. methane, ethanol and glycerol:

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where x , the ratio of CO_2 to bio-glycerol in Equation (3) can take any value between 0 and 5. In all cases, the composition of the product syngas is also affected by the water-gas-shift reaction (WGS):

Figure 4. Calculated equilibrium conversion of bio-derived feedstocks (*viz.* methane, bio-ethanol and bio-glycerol) and CO_2 and equilibrium yield of H_2 , CO and carbon, when coking is completely hindered (top) or unhindered (bottom). The blue, red, yellow, purple and green lines represent fuel conversion, CO_2 conversion, H_2 yield, CO yield and carbon yield, respectively. In the case the dry reforming of glycerol (DRG), a CO_2 : glycerol ratio of 1 is used. In the case of DRG with coking, the CO_2 conversion reaches below zero, implying more CO_2 is produced than fed, doing to the water-gas-shift reaction.

Because of the existing review articles dedicated to the dry forming of methane (DRM), *e.g.* Ref. [25,26], we only present a brief discussion in the context of CCU, *i.e.* when bio-methane (from biogas and landfill gas) is used as the feed. The analysis by Artz *et al.* suggests that, each metric ton of bio-syngas produced by an optimized DRM process has a CO_2 abatement potential of 0.52 t- CO_2 , whereas 1 t of syngas produced from fossil fuels has a positive CO_2 footprint of 1.5 t.^[23] In 2017, the global production in biomethane has reached 3 billion m^3 ,^[27] which represents a substantial potential for CO_2 utilization. Figure 4 plots the equilibrium conversion of CO_2 and various biofuels with and without carbon deposition. From Figure 4, we see that, the high endothermicity of DRM limits the conversion at low temperatures. To obtain high single-pass syngas yields, DRM should be conducted above 800 °C. For industrial production, DRM may be carried out in a facility similar to a commercial steam reformer or using the novel reactor designs described in Section 4. Carbon deposition (coking) is arguably the predominant factor preventing the large-scale deployment of DRM. Therefore, the majority of the recent researches on DRM catalysts focus on the complete elimination of coking.

Bio-ethanol, which was produced at 103 million m^3 in 2017,^[28] can be derived from biomass sources such as wood wastes and agricultural crops.^[29] Therefore, the dry reforming of bio-ethanol (DRE), is a scalable and sustainable means to reduce CO_2 emissions.^[30] DRE is more endothermic than DRM and can achieve near 100% conversion at temperature as low as 500 °C (see Figure 4). At high temperatures, ethanol spontaneously and rapidly decomposes to methane, acetaldehyde, ethylene, *etc.*, which are subsequently reformed to syngas.^[31] Similar to DRM,

carbon deposition presents a major challenge to the process stability of DRE. On the other hand, because bio-ethanol is a highly functional molecule, using it to produce syngas may not be the most cost-effective option *cf.* its direct use as a bio-fuel or its catalytic conversion to C_{2+} chemicals.^[32] Therefore, comparative technoeconomic and life cycle analyses are required to verify the benefits of adopting DRE over competing applications which use bio-ethanol.

Glycerol is a by-product of biodiesel production and accounts for ~10 wt.% of the product mixture from the trans-esterification of animal-based or vegetable oils in the presence of methanol or ethanol.^[33] Owing to the high demand for renewable transportation fuels, the production of biodiesel will continue to grow, accompanied by a rise in bio-glycerol production.^[34] In 2020, the global supply of glycerol is projected to reach 7.5 Mtpa.^[35] Therefore, the effective utilization of bio-glycerol beyond its present applications in the chemical industry is of great practical interest.^[36,37] As a biomass-derived feedstock, bio-glycerol can be used in the dry reforming process (DRG) to convert CO_2 to syngas.^[38] Because of the high oxygen content of the glycerol molecule, DRG has an equilibrium conversion of 100% even at room temperatures. The addition of CO_2 reduces the H_2 :CO ratio in the product due to RWGS. When carbon deposition is completely unhindered, the substrate conversion and product yield of DRG follow the same trend as those of DRM and DRE, as exemplified by Figure 4 for the case of CO_2 :glycerol feed ratio of 1. The equilibrium conversion and yield, calculated at other CO_2 :glycerol ratios, are shown in Figure S1 (Supporting Information). Like in other dry reforming processes, carbon deposition is severe, especially at low reaction temperatures. Also, similar to the case

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of bio-ethanol, the use of bio-glycerol for syngas production over competing bio-glycerol valorization processes (e.g. cyclic carbonates, poly-ethers, diols and epoxides) needs to be economically and environmentally justified.^[39]

The fast pyrolysis of biomass to produce bio-oil with flexible operability is considered an attractive approach to improve the energy density of biomass for storage and transportation.^[40,41] The subsequent reforming of bio-oil represents a promising and economically viable method for producing bio-syngas from mixed biomass feedstocks.^[42] Amongst the various possible process configurations, dry reforming of bio-oil (DRBO) enables the simultaneous reduction of CO₂ and valorization of biomass. Owing to the complex nature of bio-oil, the thermodynamics of DRBO is not explicitly calculated. Given the high oxygenate content of bio-oil, the thermodynamics of DRBO should follow trends similar to those of DRE and DRG (Figure 4).

2.2. Oxidative dehydrogenation of alkanes in CO₂

Light alkanes are considered abundant, low-cost and low-value components in natural gas and shale gas. Owing to their lack of chemical functionality, oil and gas industries flare large quantities of unutilized alkanes, resulting in significant CO₂ emissions. For decades, light alkane dehydrogenation has been studied as an alternative to naphtha cracking for the production of light olefins. The dehydrogenation of alkyl aromatics to aromatic alkenes is also highly industrially relevant. In fact, more than 90% of styrene is produced by the direct dehydrogenation of ethyl benzene in the presence of excess steam over an iron oxide catalyst.^[43]

Figure 5 plots the equilibrium conversion and selectivity, calculated by Gibbs free energy minimization, for the dehydrogenation of ethane, propane and ethylbenzene without

any oxidant (DDH), with stoichiometric amount of CO₂ (CO₂-ODH), and with stoichiometric amount of O₂ (O₂-ODH). At 1 atm and 600 °C (typical temperature for alkane dehydrogenation), the equilibrium yields of ethylene, propylene, and styrene by the DDH of ethane, propane, and ethylbenzene are 18%, 48%, and 41%, respectively. An oxidant, e.g. O₂ or CO₂, can remove the product H₂ and shift the equilibria of the ODH to improve alkane conversion. Contrasting O₂-ODH, which consumes the hydrogen co-product to form water, CO₂-ODH simultaneously achieves alkane dehydrogenation and CO₂ hydrogenation *via* RWGS:

In addition, the ODH of n-butane to butadiene:

also has considerable CO₂ reduction potential, given the annual demand for butadiene of 15.4 Mt.^[44]

Thermodynamically, the formation of CO by dry reforming limits the equilibrium selectivity of ethylene, propylene, and styrene to 50%, 60%, and 80%, respectively. Therefore, promoting the activation of CO₂ and suppressing the unselective C-C cleavage of alkanes are the key challenges in the development of CO₂-ODH processes amenable to large-scale implementation. Furthermore, CO₂-ODH is highly endothermic and energetically less favorable than O₂-ODH. To address this issue, Xu and Moulijn proposed hybridizing O₂-ODH and CO₂-ODH to balance the reaction heat, at the expense of compromised CO₂ abatement potential.^[22]

Figure 5. Calculated equilibrium conversion of alkanes and selectivity of alkenes for the direct, CO₂-oxidative and O₂-oxidative dehydrogenation of ethane, propane, and ethylbenzene to ethylene, propylene, and styrene, assuming no side products other than CO_x. The calculations assume zero selectivity towards undesirable side reactions e.g. partial C-C cleavage (all C-C bond cleavage reactions other than dry reforming), C-C coupling and coking.

2.3. Oxidative coupling of methane in CO₂

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An alternative means of producing ethylene is by methane coupling to ethane, followed by ethane dehydrogenation. The overall reaction, in the absence of an oxidant, is:

Similar to the dehydrogenation reactions discussed in 2.2, methane coupling can be enhanced by removing the H_2 co-product through the oxidative coupling of methane (OCM):

The oxidant will also suppress carbon formation.^[45] Thermodynamically, the formation of CO and CO_2 is overwhelmingly favored over C-C coupling. Therefore, it is crucial to develop catalysts that selectively activate only one C-H per methane molecule.^[46] Furthermore, using oxidants weaker than O_2 could potentially suppress over-oxidation and increase C_{2+} selectivity:^[47]

CO_2 -OCM brings several advantages. First, CO will be the only by-product. Second, CO_2 does not trigger gas-phase radical reactions, making it easier to control the selectivity through heterogeneous catalysis.^[47] Thirdly, the hydrogen co-product hydrogenates CO_2 in situ, thereby achieving H_2 -free carbon reduction.

2.4. Production of epoxides, cyclic carbonates and polycarbonates using CO_2

In 2010, 21,000 and 7,500 kt of ethylene and propylene were oxidized into their respective epoxides.^[21] These epoxidation processes are carried out using gas phase oxygen^[48] and emit 37 and 12 Mt- CO_2 for ethylene oxide (EO) and propylene oxide (PO) production, respectively.^[21] One way of reducing the CO_2 footprint of epoxidation is to use captured CO_2 as a soft oxidant, thereby transforming two of the top GHG emitting processes of the chemical industry into net-negative emission ones:

Reactions (13) and (14) have been less studied than other CO_2 conversion processes. The most prominent efforts have been made by RTI International, who employ a proprietary mixed metal oxide catalyst for epoxidation at 300 °C, 20 bar pressure.^[49] Additional details are provided in section 3.4.

The epoxides produced can further react with CO_2 to form cyclic carbonates and polymers, further enhancing the CO_2 -abatement potential of this synthesis pathway. Utilizing CO_2 as a comonomer in polymer production can potentially offset 10-50 Mtpa- CO_2 equivalents.^[5] Many of these cyclo-addition and polymerization reactions have already been widely deployed at commercial scale.^[2,22] Cyclic carbonates are used as polar aprotic solvents, electrodes for lithium ion batteries and in polymer synthesis. Given the low demand for cyclic carbonate production compared to the bulk chemicals, these reactions are more

suitable for transforming more decentralized sources of CO_2 into high-value products.

2.5. Direct coupling of CO_2 to alkanes to form carbonyls

C_{2+} carbonyls can be synthesized from syngas, e.g. via methanol. Despite the high TRL, the syngas-based synthesis route is energy intensive, hydrogen demanding and emits copious amount of CO_2 .^[6] Alternatively, carbonyl compounds can be synthesized by directly coupling of CO_2 to alkanes and alkenes in a single process. This type of reactions have been discussed by Otto et al.^[3] Amongst the bulk chemicals that are traded as commodities, acetone, acetic acid and acrylic acid can be produced from direct CO_2 coupling by:

With an atom economy of 100%, these reactions represent unique opportunities to synthesize functional chemicals from captured CO_2 , without consuming renewable hydrogen. Thermodynamically, most direct- CO_2 coupling reactions are highly endergonic and unfavorable in conventional reactors. For example, with a 95% CO_2 and 5% CH_4 feed, the equilibrium yield of acetic acid at 727 °C and 100 atm is only 1.6×10^{-6} . Therefore, the development of the direct CO_2 coupling pathway requires (i) high performance catalysts to selectively activate C-H bonds and facilitate C-C coupling and (ii) reactor configurations that circumvent the thermodynamic limitations.

3. Catalytic systems

The development of high performance catalysts is a rate limiting step for the technological advancement of all the CO_2 utilization processes described above. In this section, we discuss the various catalytic systems, in the order from the most technological mature (viz. dry reforming) to the least (viz. direct CH_4 - CO_2 coupling). Given the wide variety of TRLs of the processes covered, we focus our discussion differently, according to the research priority for each type of reactions.

3.1. Dry reforming

Because of the large number of elementary steps involved, the catalytic mechanism of the various dry reforming reactions remains debatable.^[50] Depending on the operating conditions and type of catalyst, different rate limiting steps have been experimentally observed, further complicating the elucidation of the reaction mechanism.^[51,52] Nevertheless, it is widely understood that a high-performance dry reforming catalyst must possess excellent activity towards (i) C-H cleavage and (ii) C=O bonds activation. While many catalysts can achieve high activities, carbon deposition remains the key obstacle preventing the dry reforming technology from becoming commercially mature.

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Tables S1-S4 selectively feature the development of catalysts for the dry reforming of methane, ethanol, glycerol and bio-oil. Here, we review recent advances in improving the performance of platinum group metal (PGM) and transition metal (TM) based dry reforming catalysts with a particular emphasis on mitigating coking.

3.1.1. Noble metal catalysts

Platinum group metals (e.g. Rh, Ru, Pd and Pt) are highly active for dry reforming, with good resistance against carbon deposition, but are considered too expensive for large scale commercialization.^[26] The performance of PGM catalysts strongly depends on the size and morphology of the supported metal particles, metal-support interaction, surface reducibility and oxygen vacancy concentration.^[53] With a typical loading of about 1 wt.%, PGM particles smaller than 5 nm are desired for maximizing the density of exposed active sites while minimizing carbon deposition. Drif et al.^[54] supported Rh catalyst on M_xO_y - Al_2O_3 mixed oxides ($M = Zr, Mg, Ni, Ce, La$) for DRM and DRE. The best performing catalyst, Rh/NiO- Al_2O_3 , contained the $NiAl_2O_4$ phase, which preserved Rh dispersion by preventing the migration of Rh into the alumina support. Silva et al.^[55] investigated the performance of ceria supported Rh catalysts for DRE and observed the dissociative adsorption of ethanol on ceria, forming surface ethoxy species and bridging OH groups. The ethoxy species was then oxidized by O adatoms to form surface

acetate, while Rh promoted the demethanation of acetate to carbonate and the reforming of the CH_x species. Tavanarad et al.^[56] impregnated PGMs (Rh, Ru, Ir, Pd and Pt) on MgO stabilized Al_2O_3 (with Mg/Al ratio = 7) and reported DRG reactivity in the order: Rh > Ru > Ir > Pd > Pt. The most active catalyst, Rh/Mg Al_2O_4 , showed increased glycerol conversion from ~50% to ~90% as the temperature increased from 600 to 750 °C. Carbon deposition, often in the form of “carbon whiskers”, has been ubiquitously observed during DRG. Owing to the formation of carbon whiskers, the activity of the Rh/Mg Al_2O_4 catalyst experienced a continuous decay over 14 h of DRG at 600 °C (CO_2 :glycerol = 1, GHSV = 15 000 $cm^3 g_{cat}^{-1} h^{-1}$).

Bac et al.^[57] prepared Rh, Ni and Co catalysts supported on Al_2O_3 - ZrO_2 - TiO_2 (AZT) and found Rh/AZT was the most active, followed by Ni/AZT and Co/AZT, during DRG at 600-750 °C, with a CO_2 /glycerol molar feed ratio between 1 and 4. Both Rh/AZT and Ni/AZT showed glycerol conversions approaching equilibrium limits and reasonable stability over 72 h TOS, whereas Co/AZT suffered from deactivation due to sintering, carbon deposition and oxidation of the Co active sites. Bulutoglu et al.^[58] prepared Rh catalysts supported on CeO_2 and ZrO_2 and reported Rh/ ZrO_2 to be marginally more reactive for DRG than Rh/ CeO_2 . On the other hand, Rh/ CeO_2 was significantly more stable than Rh/ ZrO_2 , owing to suppressed carbon deposition by the more redox-active CeO_2 structure and the encapsulation of Rh particles by oxide overlayers through strong metal-support interaction (SMSI).

Figure 6. Possible reaction mechanisms for (a) ethane dehydrogenation with CO_2 on promoted Cr/SiO_2 catalysts, reproduced with permission from Ref. [116] (Copyright American Chemical Society 2019) (b) CO_2 -ODHP over CrO_x -modified mesoporous ZrO_2 catalyst, reproduced with permission from Ref [117] (Copyright Elsevier 2019) (c) CO_2 -ODHE over a $V_2O_5/Ce_{0.6}Zr_{0.4}O_2-Al_2O_3$ catalyst, reproduced with permission from Ref. [119] (Copyright Wiley-VCH 2011).

3.1.2. Transition metal catalysts

Substantial research efforts have been devoted to eliminating the use of noble metals by developing TM catalysts, most notably Ni. Although the Ni^0 sites are active towards dry reforming, flat Ni

surfaces are prone to carbon deposition and the subsequent deactivation. Minimizing the Ni particle size, e.g. below 2 nm, has been widely adopted as a strategy to mitigate carbon deposition.^[59] However, the complete elimination of carbon requires more innovative, and somewhat unconventional

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approaches. For example, Zhang's and co-workers demonstrated that atomically dispersed Ni over hydroxyapatite (HAP) are highly resistant to coking during DRM.^[60] Furthermore, doping Ce to HAP could induce strong metal-support interaction and stabilize Ni single atoms against sintering. The single atom Ni sites are also unreactive towards non-oxidative C-H bond cleavage to form surface carbon, rendering high activity and stability for 100 h TOS with negligible coking. Tang et al.^[61] prepared a $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$ catalyst consisting of two sets of single-atom sites, viz. Ni_1 and Ru_1 , which are active towards CH_4 oxidation to CO and CO_2 reduction to CO, respectively. The dual single atom sites catalyst was found to be highly active for DRM with a H_2 TOF of 73.6 s^{-1} at 560°C .

Ruckenstein et al. reported a Ni/MgO solid solution catalyst that demonstrated 91% and 98% conversion of CH_4 and CO_2 , with stable performance over 120 h.^[62,63] Other groups have also confirmed the promising performance of this Ni/MgO catalyst.^[64–66] More, recently, Song et al.^[67] reported a Ni-Mo/MgO catalyst, on which the step edges of the MgO support is entirely covered by the Ni-Mo catalyst. By doing so, the carbon deposition was completely avoided, whilst showing extremely high DRM activity over more than 850 h of continuous operation at 800°C under a GHSV of $60 \text{ L g-cat}^{-1} \text{ h}^{-1}$.

The use of redox active supports, e.g. CeO_2 ^[68] and La_2O_3 ,^[69] has been a popular strategy to mitigate carbon deposition on Ni whilst promote the activation of CO_2 and ethanol during DRE. The same strategy is applicable to other 3d metal catalysts. For example, by doping 3% La, Fayaz et al.^[70] achieved ~ 1.65 and ~ 1.34 times higher ethanol and CO_2 conversion, respectively, than the unmodified 10%Co/ Al_2O_3 . At the same time, the formation of $\text{La}_2\text{O}_2\text{CO}_3$ intermediate significantly suppresses carbon deposition. Cao et al.^[71] prepared $\text{Cu/Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and found that the metal-support interaction between Cu and the highly redox active $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ gave rise to optimal DRE activity, viz 100% ethanol conversion with H_2/CO ratio close to unity at 700°C over 90 h TOS.^[72]

The performance of Ni catalysts, when supported on oxide materials, e.g. Al_2O_3 , MgO, MgAl_2O_4 , SiO_2 , ZrO_2 , and CeO_2 , during DRG were reviewed in detail by Kawi and Kathiraser.^[25] Again, carbon formation, often in the form of carbon whiskers, is the key catalyst design challenges for DRG.^[56,73,74] Strategies to suppress carbon deposition include using basic oxides^[74–76] and redox active supports, e.g. La-doped Al_2O_3 .^[77–79] The activity, stability and coke resistance of Ni-based DRG catalysts can be further promoted by doping noble metals. For example, Arif et al.^[38] doped Ni/CaO with Re to increase the surface acidity, reduce the formation of carbon whiskers and enhance the adsorption of glycerol, at the expense of reduced surface area and loss of porosity. Their 5% Re-Ni/CaO catalyst achieved 61% glycerol conversion and 56% hydrogen yield at 800°C under a gas-hourly space velocity (GHSV) of $3.6 \times 10^4 \text{ h}^{-1}$. Harun et al.^[80] decorated the surface of a Ni/ SiO_2 catalyst with Ag, which promoted the dispersion of NiO and enhanced DRG activity. Similar promotional effects were observed on Ag-doped 15%Ni/ Al_2O_3 , which showed improved hydrogen yield and glycerol conversion of 26.29% and 33.41%, respectively, cf. 10.18% and 13.07% of the undoped 15%Ni/ Al_2O_3 .^[81]

Ni is also the catalyst of choice for the dry reforming of bio-oil,^[82,83] given their high activity in the decomposition of oxygenated hydrocarbons.^[84–86] A simple Ni/ Al_2O_3 catalyst is capable of dry-reforming model bio-oil compounds (viz. acetic acid, phenol,

ethanol and acetone) at 700°C , achieving high hydrogen yield and bio-oil conversion of 88.19% and 96.87%, respectively.^[87] Filamentous carbon, graphitic carbon and amorphous carbon were ubiquitously observed on the surface of the spent catalyst, whilst amorphous carbon covering the active sites was identified as the dominating mode of catalyst deactivation.^[88] Although some activity could be recovered by regenerating the coked catalyst in CO_2 , steam or air, deactivation could be fundamentally mitigated by developing coke-resistant catalysts. To this end, knowledge in eliminating coking during DRM may be highly applicable to the other dry reforming process.

3.1.3. Perovskite-based catalysts

Perovskite structured oxides display high thermal stability, compositional versatility,^[89] and host high densities of redox-active lattice oxygen. These attributes are beneficial for activating CH_4 and CO_2 , while suppressing carbon deposition.^[90] To boost the redox activity, the A sites are typically occupied by rare earth elements, e.g. lanthanides, whereas the B sites are occupied by 3d transition metals, e.g. Ni. During reaction conditions, the latter exsolve in the form of metal nanoparticles, which serve as active centers for C-H activation. The post-exsolution oxide structures act as supports as well as promoters for CO_2 activation. By controlling exsolution conditions, the size of the metal particles can be minimized to (i) maximize the dispersion of active sites, (ii) enhance synergistic interactions between the metal and the support, and (iii) suppress carbon deposition.^[91]

The most commonly studied perovskite-based dry reforming catalyst is LaNiO_3 ,^[92] whose performance can be further optimized through A-site and B-site substitution. For example, a post-exsolved $\text{LaNi}_{0.8}\text{Mn}_{0.2}\text{O}_3$ catalyst shows enhanced activity attributed to the MnO phase, which promoted CO_2 activation. On the other hand, Fe-substituted $\text{LaNi}_{0.8}\text{Fe}_{0.2}\text{O}_3$ demonstrated excellent coking resistance due to strong metal-support interaction and the alloying between Fe and Ni.^[93] Srikanth et al. introduced additional alkalinity to DRM catalysts by preparing $\text{MZr}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ with $\text{M} = \text{Ca}, \text{Sr}$ and Ba ; $x = 0$ and 0.2 .^[94] Among the catalysts, $\text{CaZr}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ showed the highest DRM activity over 500 h TOS with little deactivation (see Table S1). This superior performance is attributed Ni particle sizes of 13 nm, which promotes strong interaction between the exsolved Ni^0 sites and the Ca-based oxide support. Their study also suggested the crucial role of surface formate and hydroxyl species in suppressing the formation of NiCx species, which is a precursors and a catalyst for carbon deposition. Additional redox activities could be introduced by interfacing the perovskites with other redox-active oxide phases.^[95,96] For example, Rabelo-Neto et al. found that supporting LaNiO_3 on CeSiO_2 significantly reduced the deposition of carbon during DRM cf. unsupported LaNiO_3 , because CeSiO_2 provided additional lattice oxygen redox activity and mobility, both are key factors for inhibiting carbon formation.^[97]

3.1.4. Other types of catalysts

Some researchers experimented with unconventional catalyst designs and achieved remarkable resilience against carbon deposition. For example, Palmer et al.^[98] employed a column of molten metal alloy (65:35 mol% Ni:In) and bubbled a mixture of CO_2 and CH_4 through the column. The molten alloy bubble

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column reactor facilitated simultaneous methane pyrolysis and DRM, producing syngas with $H_2:CO$ ratio >1 , when the feed ratio was $CH_4:CO_2 = 1$. The solid carbon co-product could be easily separated from the gaseous product and the molten metal, circumventing issues associated with carbon formation. The molten metal also served as a redox catalyst, whose metallic form and oxidic form (e.g. In and In_2O_3) reduced CO_2 and oxidized CH_4 , respectively. The $H_2:CO$ ratio of the product could be tailored by controlling the extent of methane pyrolysis, through adjusting the $CH_4:CO_2$ feed ratio, temperature, and the residence time of the bubbles. Another approach to mitigate coking was described by Thakur et al., who used V_2C MXenes as a synthesis template and created a V_2O_3 - V_8C_7 dry reforming catalyst, that have shown excellent coke resistance over 96 h TOS.^[99] Spectroscopic and kinetic studies revealed that this exceptional stability was due to a dynamic interconversion between surface oxide and carbide phases. CO_2 dissociates on the oxygen vacancies of V_8C_7 , releasing CO and oxidizing the carbide. CH_4 dissociates on the oxy-carbide surface, releasing H_2 and surface C^* . The surface C^* rapidly recombines with O^* from the oxycarbide and desorbs as CO. As such, coking is prevented by expeditious carbon removal, facilitated by the co-existence of oxide and carbide phases.

3.2. CO_2 -mediated alkane oxidative dehydrogenation

Two reaction mechanisms have been proposed, viz. (i) DDH + RWGS and (ii) the redox mechanism (i.e. Mars-van Krevelen mechanism). In mechanism (i), alkanes directly dehydrogenate to produce H_2 , which then reacts with CO_2 via RWGS. In mechanism (ii), C-H bonds of the alkane are oxidatively cleaved by surface oxygen species. The surface oxygen species are converted into water through O-H bond formation. Water desorption creates an oxygen vacancy which is subsequently replenished by CO_2 to produce CO. Because the various CO_2 -ODH reactions (ethane, propane, butane, and ethylbenzene) require similar catalysts, they are collectively discussed below. Selected catalyst developments for CO_2 -ODH reactions are summarized in Tables S5 - S8. An active CO_2 -ODH catalyst must exhibit both redox activity and appropriate acid-base properties. The former is necessary to facilitate the transfer of oxygen atoms from CO_2 to hydrocarbon substrates, whereas the latter is required to activate the hydrocarbons and CO_2 , respectively.^[15,100,101]

3.2.1. Metal oxide catalysts

Redox active oxides of transition metals, e.g. Cr ,^[102] V ,^[103,104] Fe ,^[105] Mn ,^[106] Co ^[107] and Mo ^[108] are catalytically active for CO_2 -ODH reactions. The active sites are often identified as oligomeric oxide species with high oxidation states, e.g. $Cr^{6+/5+}$,^[109] V^{5+} ,^[103,104] Fe^{3+} ,^[105] Mn^{3+} ,^[110] Co^{3+} ^[107] and $Mo^{6+/5+}$ ^[108]. Therefore, high catalyst activities can be obtained by maximizing the surface dispersion of the active MO_x species and minimizing the size of the surface MO_x clusters. Here, the dispersion not only depends on the catalyst loading, but also on the surface acidity of the supports. In general, moderate surface acidity favors CO_2 -ODH. Controlling the surface acidity is also crucial to suppress side reactions, viz. reforming and coking.^[111] Experimentally, the surface acidity of the supports can be controlled by (i) mixing insoluble or partially insoluble oxides of different acidities, e.g. SnO_2 - ZrO_2 ,^[112] TiO_2 - ZrO_2 ^[107] and TiO_2 - Al_2O_3 ^[108], (ii) preparing mixed oxide solid solutions, e.g. $Ce_xZr_{1-x}O_2$ ^[113] and (iii) changing

the Si/Al ratio of zeolite-type supports.^[109,114] It is possible, although inconclusive, that surface acidity also determines the reaction mechanism. For example, $CrO_x/\gamma-Al_2O_3$ reportedly favors the DDH + RWGS mechanism during CO_2 -ODHE,^[115] whereas Zr- and Ce-doped CrO_x/SiO_2 and CrO_x/ZrO_2 favor the redox mechanism during CO_2 -ODHE^[116] and CO_2 -ODHP,^[117] respectively, as depicted in Figure 6 (a) and (b).

The redox activity of the active sites can be further promoted by doping and interfacing with redox-active materials. For example, Ye et al.^[118] reported that doping 20% Cr_2O_3/Al_2O_3 with 5% CeO_2 renders 66.7% styrene yield and 99% styrene selectivity, owing to the ability of CeO_2 to promote the redox activity of the CrO_x catalysts. Liu et al. prepared a 6 wt% $V_2O_5/Ce_{0.6}Zr_{0.4}O_2-Al_2O_3$ (V_2O_5/CZA) catalyst for CO_2 -ODH of ethylbenzene (CO_2 -ODHEB), in which $Ce_{0.6}Zr_{0.4}O_2$ not only modulated the surface acidity, but also enhanced the redox activity of the V^{5+}/V^{4+} active sites (as shown in Figure 6 c), resulting in ~50% EB conversion and ~98% styrene selectivity over 48 h TOS.^[119]

Post-transition metal oxides, viz. Ga_2O_3 and In_2O_3 also show good performance for CO_2 -ODH, bar the strong tendency to coke.^[120,121] The active sites are considered to be the surface Ga^{3+} and In^{3+} species, which facilitate the heterolytic C-H cleavage of alkanes to surface metal hydride and metal alkoxide species.^[121,122] The activity of the Ga_2O_3 -based catalysts depends on Ga-loading,^[123] the type of Ga_2O_3 polymorphs (e.g. β - Ga_2O_3 and γ - Ga_2O_3),^[121] and the synthesis conditions.^[122] Similar to the transition metal oxides, the activity of the post-transition metal oxide catalysts can be improved by adjusting the surface acidity.^[124] For example, Chen et al.^[125] found that, amongst the various oxide supports (MO_x , $M = Al, Zn, Zr, Ti, Fe, Mg, Si$, and Ce), In_2O_3 - Al_2O_3 containing 20 mol% indium showed the highest dehydrogenation activity with superior long-term stability, giving 27% propylene yield over 12 h TOS at 600 °C.

CO_2 -ODHEB can also be catalyzed by mildly reducible metal oxides, e.g. ZrO_2 ,^[126] TiO_2 ^[127] and CeO_2 .^[128] Zhang et al. reported that the CO_2 -ODHEB proceeds via a DDH + RWGS mechanism on a high surface area CeO_2 ,^[128] whereas the computational study by Fan et al. suggests that the reaction proceeds via the redox mechanism on CeO_2 (111).^[129] The catalytic activity and the coking resistance of the mildly reducible oxides can be significantly boosted by (i) doping alkali metals,^[127] (ii) forming reducible solid solutions, e.g. $Sn_{1-x}Zr_xO_2$ and $Ce_{1-x}Zr_xO_2$ ($0 < x < 1$),^[126,130] and (iii) interfacing the redox active metal oxides with secondary oxide phases of appropriate surface acidity.^[131,132]

3.2.2. Metal and metal alloy catalysts

Noble metals, e.g. Au, Pd and Ru, in their metallic form, can serve as co-catalysts to the redox-active metal oxides.^[133,134] Jin et al. found that, doping 1 wt.% Ru to a CrO_x/SiO_2 catalyst promoted CO_2 activation and removal of hydrogen adatoms generated by C-H cleavage, resulting in a two-fold enhancement in propylene yield over undoped CrO_x/SiO_2 .^[135] However, high loading (3 wt% Ru) led to high surface coverage of CO_2 , which competed with the adsorption of propane. Nowicka et al. performed a temporal analysis of products during CO_2 -ODHP on $Pd/CeZrAlO_x$, and reported a redox mechanism over the Pd/CeO_2 interface, where Pd catalyzes the redox reaction of the Ce^{4+}/Ce^{3+} couple, as depicted in Figure 7 (a).^[136] In this case, the Pd/CeO_2 interface could be maximized at an optimal Pd loading of 5 wt%, which corresponds to a mean Pd particle size of 17 nm.

Figure 7. (a) Schematic mechanism for the CO₂-ODH of propane on a 5% Pd/CeZrAlO_x catalyst, reproduced with permission from Ref [136] (Copyright American Chemical Society 2018) (b) The Mars-van Krevelen redox mechanism for the ODH of butane over the O-Mo terminated {110} facet of the NiMoO₄ catalyst in a CO₂ or N₂O atmosphere. Bold numbers are activation barriers in kJ mol⁻¹, reproduced with permission from Ref. [104] (Copyright Royal Society of Chemistry 2017). DFT calculated energy profiles for the oxidative C-H and C-C bond scission pathways. (c) Bulk Fe₃Ni(111) surface, (d) Pt-terminated Ni₃Pt(111) surface, and (e) FeO/Ni(111) interface as well as the optimized geometries of (f) CH₃CH₂CH₂O and (g) CH₃CH₂CH₂ on FeO/Ni(111), reproduced with permission from Ref [139] (Copyright Springer Nature 2018).

Chen and co-workers screened, experimentally and computationally, bimetallic alloys supported on CeO₂ for CO₂-ODH of light alkanes. They found Fe₃Ni₁/CeO₂ to be the best bimetallic catalyst.^[137–139] CeO₂ facilitates the direct C=O scission of CO₂, whereas the Ni-FeO_x/CeO_x interfacial sites catalyze selective C-H cleavage to produce ethylene. DFT calculations suggest that the Fe-O species on Fe₃Ni₁(111) favors the selective, oxygen-mediated C-H cleavage to form *CH₃CHCH₂ + H₂O, whereas other metal alloys, e.g. Ni₃Pt₁(111), favor C-C cleavage

to form *CH₃CH₂ + *CO, as depicted in Figure 7 (c)-(g). The performance of Fe₃Ni₁ can be further improved by enhancing the redox activity of the support, e.g. by forming a CeO₂-ZrO₂ solid solution.^[140]

Dasireddy et al.^[104] studied a commercial Ni-Mo/Al₂O₃ catalyst for CO₂-ODHB and N₂O-ODHB and attributed the high butadiene selectivity (80%) to the lack of electrophilic oxygen species, which favors the over-oxidation of alkenes to carbon oxides. Indeed, DFT calculations (shown in Figure 7 b) suggest that ODHB

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proceeds via a redox mechanism involving surface Mo-O species, whereas over-oxidation to CO_x takes place on surface Ni-O species. However, butadiene was also a precursor to coke formation. Thus, high butadiene selectivity correlates well with the high rate of coking.

3.2.3. Other types of catalysts

There are also reports of CO_2 -ODH catalyzed by non-oxidic active sites. For example, Wang et al. catalyzed CO_2 -ODHEB using carbon-coated alumina and achieved 32% EB conversion and 95.6% styrene selectivity at 550 °C, when the carbon loading was 17 wt%. The active sites were identified as surface carbonyl groups.^[141] More recently, a metal-free BN catalyst with nearly uniform mesopores of ~22 nm for CO_2 -ODHEB was found to be active for CO_2 -ODHEB.^[142] Both DFT calculations and experimental results suggest that the edge boron atoms are the active sites for CO_2 activation. The oxygen in the B-bonded CO_2 (>B-OCO) subsequently reacts with the α/β hydrogen of the EB molecule, forming >BOH and a desorbed CO. The BN catalyst prepared at 900 °C in Ar exhibited the highest CO_2 -ODHEB activity (viz. 21% EB conversion and >95% styrene selectivity), whereas BN catalysts prepared at higher temperatures and, or in reducing atmospheres were less reactive, because of the reduced amount of edge -BO_x sites.

3.2.4. Factors controlling the selectivity of oxidative dehydrogenation

Based on the discussion in the preceding sections, we identify general design principles for oxidative dehydrogenation of alkanes, as illustrated in Figure 8. In the case of oxide-based redox catalysts (e.g. CrO_x), the activation of alkane (step a) is facilitated by the reduction of a high valent cation (e.g. Cr^{6+} to Cr^{3+}), sometimes accompanied by the removal of a lattice oxygen (i.e. the Mars-van Krevelen mechanism, step b). The high valency and the lattice oxygen vacancy are subsequently restored via CO_2

reduction to CO (step d). In other catalytic systems, e.g. in the case of Ga_2O_3 ,^[121,122] the dehydrogenation of alkanes proceeds via heterolytic C-H cleavage, followed by RWGS over the catalyst surface. Since both the active sites and the support materials are oxidic, chemical interaction at the oxide-support interface, and the resulting modifications of the active sites are inevitable. Therefore, the structure of the oxide support is as important as that of the active components.^[15]

During CO_2 -ODH, Lewis acidity is required to draw electrons from the alkane substrate to the catalytic surface, whereas Lewis basicity is required to extract hydrogen from the substrate and to activate CO_2 by donating electrons to the antibonding orbital of CO_2 .^[100] In addition to acid strength, the inherent reactivity of metal atoms also dictates dehydrogenation selectivity. For instance, while the O^* assisted C-H dehydrogenation is catalyzed by Fe_3Ni_4 , unselective C-C dissociation occurs on more reactive metal sites like Ni_3Pt_1 . Therefore, the acid strength and chemical environment around the transition metal active sites are important metrics for suppressing unwanted C-C dissociation. In general, weak acidity favors the selective dehydrogenation to alkenes, whereas strong acidity favors the undesirable C-C cleavage and carbon deposition (step e). The use of oxide solid solutions, mixed oxides and zeolites supports with adjustable cationic compositions are all accessible means to tune the acid-base properties of the catalyst to achieve optimal performance.

It is encouraging to see that the catalyst design strategies described above yield high alkene selectivity, whilst carbon deposition has been mitigated by enhancing the surface basicity and increasing the oxygen mobility of the support. Recent advances notwithstanding, carbon deposition remains ubiquitously severe on all the CO_2 -ODH catalysts studied. Overall, it is necessary to mitigate carbon deposition on both the active sites and the supports.^[143] We extensively discussed approaches to mitigate carbon deposition in section 3.1. Such approaches are also applicable to oxidative dehydrogenation, and should be key avenues of future research.

Figure 8. Catalyst design principles for oxidative dehydrogenation catalysts using CO_2 as an oxidant. (a) C-H activation together with metal center reduction on moderately strong Lewis acid sites. (b) OH^* s recombine forming water, whose desorption creates oxygen vacancies (c) Since C-C bonds are preserved during selective dehydrogenation, less reactive metals are employed. More reactive metals cleave C-C bonds, suppressing selectivity (d) Oxygen vacancies are re-oxidized by CO_2 . (e) Strongly Lewis acidic sites promote deep dehydrogenation and cracking (reduces dehydrogenation selectivity), and oligomerization (promotes coking). Sintering and coke deposition are controlled by optimizing the metal nanoparticle size and adhesion to the oxide support.

3.3. Oxidative coupling of methane using CO_2

In comparison with dry reforming and oxidative dehydrogenation reactions, C-C coupling is challenging, primarily because the

coupling products are more easily oxidized by CO_2 than the reactants. For instance, selective C-H cleavage and suppressing side reactions such as over-oxidation and carbon deposition require specifically tailored surface oxygen species. These

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requirements can be facilitated by bifunctional oxide-oxide interfaces with redox activity and surface basicity for CO₂-OCM. The redox active metal oxides serve as the active sites for CO₂ activation, whereas the basic sites such as Ca²⁺ steer the selectivity towards C-C coupling.^[144] For example, Wang et al. reported CaO-CeO₂,^[144] CaO-Cr₂O₃^[145] and CaO-ZnO^[146] to be promising CO₂-OCM catalysts, showing 3.2% - 4.3% C₂ yield at 850-875 °C. Other studies suggested the need for catalysts having stronger surface basicity than CaO. For instance, Wang and Ohtsuka studied CaO-MnO₂, SrO-MnO₂, and BaO-MnO₂ catalysts, and found SrO-MnO₂ and BaO-MnO₂ catalysts to exhibit higher C₂ selectivity than CaO-MnO₂ at 700-900 °C.^[147] At 900 °C, the SrO-MnO₂ catalyst provided the highest C₂ yield of 6.3% with 64% C₂ selectivity. The active sites are the Mn³⁺ species in SrMnO_{2.5} and BaMnO_{2.5}. In contrast, the CaO-MnO₂ catalyst mostly contained Mn²⁺, which has low redox activity. Cai et al.^[148] investigated Mn/SrCO₃ catalysts with Mn:Sr ratios of 0.1 and 0.2, and achieved C₂ selectivity of 88% and 79%, with C₂ yields of 4.3% and 4.5%, respectively. They also suggested the role of SrCO₃ in supplying CO₂ to the redox active sites.

Recent advances in catalyst development for CO₂-OCM are summarized in Table S9. Notably, Istadi *et al.*^[149] prepared alkali (Li₂O), alkaline earth (CaO), and transition metal oxide (WO₃ or MnO) doped, MgO-based and CeO₂-based catalysts. 2%Li₂O/MgO showed the highest performance (*viz.* 98% C₂₊ selectivity and 5.7% C₂₊ yield), which was attributed to the presence of the Li₂O₂ peroxide species. 5%MnO/15%CaO/CeO₂ was found to be the optimal formulation for the CeO₂-based catalysts, in which the MnO dopant promoted both the oxygen mobility and the formation of oxygen vacancies on CeO₂, resulting in enhanced redox activity. Their study also correlated surface lattice oxygen and bulk lattice oxygen to CH₄ coupling activity and CO_x production, respectively. All of the oxide-based CO₂-OCM catalysts contain substantial fractions of basic oxides and redox-active oxides (*i.e.* more than 10 wt.% each). Therefore, improving the dispersion of oxide particles is an effective means to maximize the catalytic activity. More recently, Zhang et al.^[150] prepared a transition-metal free, Cl-doped CaO-based catalyst, supported on Na₂CO₃. During CO₂-OCM at 950 °C, the molten Na₂CO₃ catalyst resulted a C_{2,3} yield of 6.6%. This presents a potential to catalyze CO₂-OCM using only earth abundant elements, provided that practical issues such as metal evaporation can be successfully solved. Despite the significant improvements in the catalysts' performance over the years, the yields of C₂₊ products (a few percent) remain low compared to the aspirational target of ~30% for commercial application.

3.4 Production of epoxides, cyclic carbonates and polycarbonates using CO₂

3.4.1. CO₂-epoxidation

CO₂-epoxidation begins with C-O dissociation at an oxygen defect. The oxygen adatom occupying this defect combines with ethylene forming ethylene oxide (EO). The overall selectivity is affected by parasitic C-C/C-H dissociation that combusts ethylene to form CO₂ and H₂O. Bench-scale catalytic tests on mixed-metal oxides developed by RTI revealed ethylene oxide yields between 5% to 7.5%, which are slightly lower than the commercial catalysts such as Dow METEOR (~13%) and Shell Omega (~11%).^[49] The catalyst suffered from deactivation and needed to be regenerated

between cycles. These studies indicate that an ideal CO₂-epoxidation catalyst has two key attributes. First, sufficient oxygen vacancies to activate C-O bonds in CO₂. Second, moderately strong acid sites which are relatively inactive towards C-H/C-C dissociation of ethylene to promote the selectivity towards epoxide. Despite the lower selectivity, a life cycle analysis by RTI showed that using CO₂ as a soft oxidant resulted in 2.82 t-CO₂ avoided per t of ethylene oxide produced.^[49] These interesting results demonstrate the potential for using CO₂ as an oxidant for alkene epoxidation. Further studies are needed to understand catalyst deactivation and design highly selective mixed metal oxides that preserve C-H bonds while forming C-O bonds. Ethylene oxide and propylene oxide have widespread applications in synthesizing cyclic carbonates and polycarbonates, which are discussed in the following sections.

3.4.2. Cyclic carbonates and polycarbonates

We briefly overview the active site requirements for synthesizing cyclic carbonates with a specific emphasis on a new class of heterogeneous catalysts that do not require stoichiometric quantities of co-catalysts. This discussion complements the extensive review by Della Monica and Kleij on the catalytic conversion of CO₂ to cyclic carbonates.^[151]

Reactions between epoxides and CO₂ have traditionally been catalyzed by homogeneous catalysts *e.g.* Inoue's aluminum-porphyrin complex.^[152] The electrophilic metal cations activate the epoxide linkages, whereas a nucleophilic co-catalyst is needed to activate CO₂. The CO₂-nucleophile complex, in turn, attacks the activated epoxide. Cyclic carbonates are formed through intramolecular cyclic elimination. These reactions are typically performed at high pressures (~6-20 MPa), and temperatures between 80 and 160 °C, in a solvent.^[153]

The central challenge in catalyst design is to discover catalytic architectures that are easily recoverable, co-catalysts-free, and active under lower pressures in solvent-free environments. Several efforts have focused on immobilizing bifunctional homogeneous catalyst analogs on heterogeneous supports to meet the above requirements.^[154–158] The bifunctional catalysts contain both electrophilic (Lewis acid) and nucleophilic (Lewis base) functions, thereby avoiding the use of a co-catalyst. Such catalysts can be prepared by (i) anchoring organometallic complexes on heterogeneous supports,^[155,156] (ii) encapsulating these complexes within large pore zeolites,^[157] and (iii) tailoring the ligands of metal organic frameworks (MOFs).^[154] For example, Yang *et al.* showed that Mg-MOF-74 could both capture CO₂ and convert it to cyclic carbonates in 20 atm and 373 K.^[154] They hypothesized that the open Mg atoms functioned as electrophiles while the oxygen atoms of the organic linkers had sufficient basicity to convert adsorbed CO₂ to a nucleophile. Hence, no co-catalyst was needed. The ability of MOFs to combine CO₂ adsorption from dilute streams (*e.g.* CO₂/N₂), and CO₂ conversion in one system makes it possible to achieve process intensification for chemical production from decentralized CO₂ sources which are otherwise difficult to purify. However, the stability of MOF-based materials for cyclic carbonate synthesis needs to be exhaustively studied.

There are similarities in catalytic active site requirements for cyclic carbonate production and dry reforming, dehydrogenation, oxidation. For all reactions, CO₂ is activated on electron rich oxygen vacancies through either O=CO dissociation or

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transforming CO_2 into a strong nucleophile. On the other hand, C-H dehydrogenation and ring opening of epoxides occur on Lewis-acidic metal centers. Thus, catalyst design rationales already established for dry reforming, dehydrogenation, and oxidation can, in principle, be directly transferred to cyclic carbonate production. CO_2 is also extensively used as a co-monomer in polymer synthesis. The reaction mechanisms for CO_2 -based

polymerization are extensively discussed by Lu et al.^[153] and Mulchandani et al.,^[159] while a general overview of the slate of polymers already being produced in industry using CO_2 is presented by Burkart et al.^[2] Incorporating captured CO_2 into polymers is thus an industrially attractive, relatively high TRL process for valorizing decentralized CO_2 sources.

Figure 9. (a) Reaction scheme for the direct conversion of carbon dioxide and methane to acetic acid over Cu-modified zeolites, reproduced with permission from Ref. [165] (Copyright Royal Society of Chemistry 2019). (b) Scheme of mechanistic steps involved in acetic acid formation from CH_4 and CO_2 over CeO_2 -ZnO/MMT catalyst and (c) Energy profiles of acetic acid formation on $\text{CeO}_2(111)$ and $\text{ZnO}(10\bar{1}0)$. Black and red lines indicate the reaction pathways on $\text{CeO}_2(111)$ and $\text{ZnO}(10\bar{1}0)$, respectively, reproduced with permission from Ref [166] (Copyright Elsevier 2018). (d) Catalytic cycle of the production of CH_3COOH from CH_4 and CO_2 via Zn-doped ceria catalyzed C-C coupling, reproduced with permission from Ref. [167] (Copyright American Chemical Society 2016). (e) Energy profile from $\text{CH}_4(\text{g})$ and $\text{CO}_2(\text{g})$ to $\text{CH}_3\text{COOH}(\text{g})$ on the $(\text{ZnO})_3/\text{In}_2\text{O}_3(110)$ surface, reproduced with permission from Ref. [168] (Copyright American Chemical Society 2019).

3.5. Direct coupling of CO_2 to alkanes to form carbonyls

The most fundamental C-C bond forming reaction involving CO_2 , is the synthesis of oxalic acid through CO_2 dimerization. Oxalic acid produced from CO_2 can be used as an intermediate to synthesize high volume bulk chemicals, e.g. ethylene glycol (20,000 ktpa).^[21] CO_2 dimerization to oxalic acid is almost entirely

performed using homogeneous^[160] or heterogeneous electrochemical systems.^[161] One potential way of avoiding direct hydrogen input is to use hydrogen generated through biomass oxidation (e.g. glycerol) reactions occurring at the anode. Pairing biomass oxidation with oxalic acid production can also be potentially advantageous from a techno-economic standpoint. Recent studies have shown that organic oxidation reactions occur

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at lower overpotentials than oxygen evolution, whilst simultaneously generating higher value products than O_2 .^[162] Burkart et al. also extensively discussed the use of CO_2 as an oxidant for synthesizing higher carboxylic acids produced at large scales (e.g. benzoic acid, acrylic acid, methacrylic acid).^[2] To complement their discussion, we describe the catalytic synthesis of acetic acid and acetone from CO_2 and CH_4 .

While there have been reports of homogeneously catalyzed CH_4 - CO_2 coupling,^[163,164] heterogeneous catalysts are preferred for large scale production. One such example is the synthesis of acetic acid via CH_4 - CO_2 coupling over PGMs (Pd, Pt, Rh), 3d TMs (Cu, Co, Zn, and Mn) metal clusters confined on zeolites, and bifunctional mixed metal oxides containing uniformly dispersed Lewis acid and Lewis base sites. However, because of the low yields, most studies focus on mechanistic aspects. To circumvent thermodynamic limitations and maximize product yield, catalysts were exposed to alternating feeds of CH_4 and CO_2 , whilst the products are examined by surface-sensitive characterization techniques.

For example, Wang *et al.* found that binuclear copper-oxo cluster ($[CuO_2Cu]^{2+}$) in the three-dimensional BEA and MFI zeolites and trinuclear copper-oxo cluster ($[Cu_3(\mu-O)_3]^{2+}$) in the one-dimensional MOR and TON zeolites are the active sites for acetic acid synthesis, as shown in Figure 9 (a).^[165] Shavi *et al.*^[166] prepared MMT (montmorillonite)-supported single and dual active site catalysts containing ZnO , MnO_2 , and CeO_2 , amongst which CeO_2 - ZnO /MMT showed promising catalytic performance. DFT calculations revealed that CH_4 and CO_2 are preferentially adsorbed on ZnO and CeO_2 , respectively, thereby avoiding the competition between the two adsorbates (Figure 9 b). At the Zn - CeO_2 interface, CeO_2 sites facilitate the adsorption and surface migration of CO_2 , whereas the formation of acetic acid is favored on ZnO (Figure 9 c), which forms a Zn -C bond with the activated methyl group, preventing it from further dehydrogenation (Figure 9 d).^[167,168] Then, CO_2 is inserted into the Zn -C bond in an activated bent configuration, via a three-centered Zn -C-C transition state moiety with an activation barrier of 0.51 eV. The resulting surface acetate group desorbs upon protonation. The same researchers also simulated CH_4 - CO_2 coupling on ZnO/In_2O_3 , Ga_2O_3/In_2O_3 and ZrO_2/In_2O_3 interfaces and found the reaction follows Langmuir-Hinshelwood mechanism.^[168] $(ZnO)_3/In_2O_3(110)$ exhibited the highest activity, with the Zn -O pair serving as the active center for C-H activation and the oxygen vacancies on $In_2O_3(110)$ as the active sites for CO_2 activation. Bader charge analysis suggests synergy between the activation of CH_4 and CO_2 , i.e. the presence of a CO_2 adsorbate reduces the energy barrier for CH_4 dissociation at an adjacent ZnO site, as shown in Figure 9 (e). Microkinetic modelling showed that the acetic acid formation rate is 1st order with respect to CH_4 but 0th order with respect to CO_2 , meaning that that methane activation is the rate-limiting step.

On both metal-exchanged MFI zeolites^[165] and CeO_2 -supported metal oxides,^[167,168] the electronegativity of the cationic sites are revealed as the catalytic descriptor, which determines the energy of the lowest unoccupied molecular orbital and, in turn, the energy barrier of the rate limiting step, viz. C-H activation. Therefore, low electronegativity species (e.g. Zn) favor C-H activation, whereas high electronegativity species (e.g. Ni) favor dry reforming. This trend in selectivity is analogous to the above discussion on dry reforming versus dehydrogenation in section 3.2.

Going beyond acetic acid, Ge's group mapped out a mechanism for acetone synthesis via CO_2 and CH_4 coupling over Zn -doped CeO_2 , i.e. the C-C coupling between CO_2 and surface-stabilized CH_3^* to form surface acetate, followed by further coupling with one more neighboring CH_3^* .^[169] Their DFT calculations show the feasibility of achieving CO_2 -based carbon chain growth over active site ensembles constructed on a CeO_2 -based catalyst. The coupling of the acetate species with the methyl moiety follows a nucleophilic addition mechanism, with apparent activation energies of 0.25 and 0.14 eV on an oxygen vacancy and on neutral surfaces, respectively. In all cases, the reliance on mixed oxide interfaces to achieve high CO_2 - CH_4 coupling activity means that an ideal catalyst structure should contain high surface concentration of desired interfacial sites.

4. Reaction engineering approaches

While optimizing the catalyst design can significantly improve the conversion and selectivity of the CO_2 utilization reactions discussed above, the energy efficiency of these chemical processes may be further improved by the reaction engineering approaches discussed below.

4.1. Membrane reactors

Several CO_2 reduction reactions discussed above integrate alkane oxidation and CO_2 reduction within a single process. This integration results in more complex product mixtures than the case when O_2 is used, because CO and CO_2 will always be simultaneously present in the product mixtures. At a process level, the need to separate alkenes and unconverted alkanes from CO_x means additional parasitic energy penalty. Therefore, process intensification approaches that inherently achieve product separation, such as membrane reactors, are attractive solutions for further improving process efficiency. Since the 1990s, packed bed membrane reactors (PBMR) have been investigated for boosting the alkene yields of alkane dehydrogenation.^[170,171] By selectively removing the hydrogen produced through catalytic oxidation and, or inert gas sweeping on the permeate side, a chemical potential gradient across the membrane is established. This gradient can continuously drive the membrane reaction process, as long as sufficient heat is supplied to maintain the reaction temperature. The PBMR model by Dangwal *et al.* predicts a maximum ethane conversion of 98% at 600 °C and 3.5 atm retentate pressure,^[172] far exceeding the equilibrium conversion of 17.7% in a fixed-bed DDHE setup. In the case when an oxidant is supplied to the other side of the membrane, the membrane reactor can essentially facilitate ODH with inherent product separation. For CO_2 -ODH reactions, either hydrogen permeable membranes or oxygen permeable membranes can be used,^[173] as illustrated in Figure 10 (a) and (b).

In a hydrogen permeable membrane reactor system, the retentate side facilitates the catalytic alkane dehydrogenation, whereas the CO_2 (permeate) side can be decorated with selective hydrogenation catalysts, to enable the formation of C-H bonds via CO_2 hydrogenation. This design presents an advantage over CO_2 -ODH performed in fixed-bed reactors, in which the selectivity of CO_2 hydrogenation is limited to CO . Pati *et al.* demonstrated this concept using a bifunctional membrane reactor, fabricated from a Al_2O_3 hollow-fiber substrate. One side of the hollow fiber

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was coated with a layer of $\text{Pd}_{57}\text{Cu}_{43}$ alloy and served as both a H_2 membrane and a propane dehydrogenation catalyst, whereas the other side of the membrane was loaded with 10% $\text{Ni/Ce}_x\text{Zr}_{1-x}\text{O}_2$, which served as a CO_2 methanation catalyst, as depicted in Figure 10 (a).^[174] The membrane reactor achieved higher CO_2 conversion (76%) than an equivalent fixed bed reactor (~72%) at 350 °C. The hydrogen consumed by the methanation reaction enhanced the flux across the membrane, leading to a hydrogen recovery rate of up to 75%.

An oxygen permeable membrane reactor system can be functionalized to facilitate CO_2 reduction and ODH on the CO_2 side and the alkane side, respectively, as shown in Figure 10 (b). To date, CO_2 -ODH conducted in an oxygen permeable membrane reactor is yet to be reported. Nevertheless, oxygen permeable membrane reactors have been applied by several groups for H_2O -ODHE. For instance, Jiang *et al.* used $\text{BaCo}_x\text{Fe}_y\text{Zr}_{1-x-y}\text{O}_{3-\delta}$ hollow-fiber membranes for H_2O -ODHE and achieved 59% ethane conversion and 89% ethylene selectivity at 800 °C.^[175] Dimitrakopoulos *et al.* used a cobalt-free, $\text{BaFe}_{0.9}\text{Zr}_{0.1}\text{O}_{3-\delta}$ perovskite membrane reactor for H_2O -ODHE and achieved 95% ethane conversion and 83% ethylene selectivity at 900 °C.^[176] Given the thermodynamic similarity between H_2O splitting and CO_2 splitting at 800–1000 °C, it is reasonable to expect ceramic membrane reactors to achieve similar performance for CO_2 -ODHE under comparable conditions. Oxygen permeable ceramics can also be used to fabricate membrane reactors capable of facilitating biofuel dry reforming and CO_2 -OCM with inherent product separation.^[177] Despite the lack of reports dedicated to membrane reactors for CO_2 -OCM, membrane reactors has been studied for O_2 -OCM since the

1990s.^[178] Because of the high operating temperature of oxygen permeable membranes, there exist potential engineering challenges associated with the mechanical and chemical stability of the membranes over prolonged high-temperature operations.^[175]

The use of CO_2 permeable membrane could remove the need for a standalone CO_2 capture process and eliminates the additional energy penalty associated with it (Figure 10 c). Zhang *et al.* used an O^{2-} - CO_3^{2-} bi-ionic membrane to perform CO_2 -ODHE over a Cr_2O_3 -ZSM-5 catalyst.^[179] The diffusion of O^{2-} and CO_3^{2-} is facilitated by Gd_2O_3 -doped CeO_2 and an eutectic mixture of molten Li_2CO_3 and Na_2CO_3 , respectively. The author reported >90% C_2H_6 conversion, ~60% CO_2 conversion and ~80% C_2H_4 selectivity using this membrane reactor design; such performance was substantially superior over those reported in a single-pass fixed-bed reactor (see Table S5). Although the literature generally reports favorable performance of lab-scale membrane reactors (the studies cited above are by no means an exhaustive summary), the heat management aspects is also critical to large-scale deployment. The reactor model by Choi *et al.* showed a temperature drop of up to 100 °C along a 5 m hollow fiber membrane reactor bundle during propane dehydrogenation.^[180] The analysis by Dittich suggests that heat supply is the rate-limiting factor for propane dehydrogenation in commercial-scale membrane reactors.^[181] To address the heat demand by alkane dehydrogenation, Brune *et al.* proposed a hybrid system, in which endothermic dehydrogenation reactions and the exothermic O_2 -ODH reactions are conducted on different sides of a membrane, to make the overall process thermal-neutral.^[182]

Figure 10. (a) – (c) membrane reactor design for CO_2 -ODH of alkane using hydrogen permeable membranes, oxygen permeable membranes and CO_2 permeable membranes, respectively. (d) chemical looping reactor design for CO_2 -driven oxidative partial oxidation of hydrocarbons. (e) schematic of a directly irradiated annular pressurized receiver (DIAPR) solar reactor, reproduced with permission from Ref. [214] (Copyright Royal Society of Chemistry 2007). (f) a schematic comparison of the radial temperature profiles between a gas fired methane reformer and an electrically heated methane reformer, reproduced with permission from Ref. [218] (Copyright AAAS 2019)

4.2. Chemical looping

The fundamental principle of chemical looping is analogous to an oxygen permeable membrane reactor, i.e. the oxidation of hydrocarbons and the reduction of CO_2 take place in separate reactors. The oxygen transfer between the two reactors is

facilitated by the uptake and release of the lattice oxygen of oxide materials. In the case of chemical looping, the movement of lattice oxygen is achieved by physically moving the oxide materials, known as oxygen carriers, between the two reactors. As such, the hydrocarbons and CO_2 are inherently separated, as depicted in Figure 10 (d). The effectiveness of chemical looping processes

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depends on the formulation of oxygen carriers, which also act as redox catalysts. For example, chemical looping O_2 -ODHE (CL- O_2 -ODHE) and CL- O_2 -ODHP have been successfully demonstrated by Na- and W-promoted Mn/SiO₂ and Mn/MgO redox catalysts.^[183] and Mo-V-O mixed oxides, respectively.^[184] More recently, Jeong et al. achieved CL- CO_2 -ODHE using a FeO₂/TiO₂ mixed oxides redox catalyst. Despite the relatively low ethylene yield (viz. 8.5% at 550 °C and 1 atm pressure), their finding signifies the feasibility of the CL- CO_2 -ODHE concept and suggests potential for further improvements through oxygen carrier design. The application of chemical looping technology to oxidative coupling of methane (CL-OCM) has also been demonstrated using the state-of-the-art OCM catalyst, Na₂WO₄/Mn/SiO₂,^[185–187] as well as a Li-doped Mg₆MnO₈ redox catalyst.^[188] For the synthesis of ethylene oxide, Chan *et al.* reported chemical looping ethylene epoxidation on a Ag/SrFeO₃ redox catalyst,^[189] without directly mixing oxygen with ethylene. The product yield and selectivity of chemical looping epoxidation was further improved by doping CeO₂ to Ag/SrFeO₃.^[190] By rationally engineering the lattice oxygen activity and the catalytic active sites, chemical looping could become a cost-effective process intensification strategy for simultaneously achieving CO₂ reduction, alkane valorization and inherent product separation.

The chemical looping approach also offers an extra degree of freedom during continuous operation, because the residence time of the catalyst in each half step can be adjusted independently. For instance, during CL- CO_2 -ODH of alkanes, the coked catalyst have a sufficiently long residence time in the CO₂ reactor (see Figure 10 d) to ensure complete catalyst regeneration via the Bourdeaux reaction. Such flexibility is also beneficial to dry reforming reactions, which can be catalyzed by 3d transition metal catalyst (e.g. Ni), on which the carbon deposited can be cyclically removed in the CO₂ reactor, thereby eliminating accumulation of coke.^[191–194] This advantage is particularly relevant to feedstocks with strong coking tendencies such as bio-oil.^[195] During CL-dry reforming, the catalysts are exposed to reacting gas mixtures different from that in conventional reformers. Therefore, the optimal catalysts formulation for CL-dry reforming also differs from that of conventional processes. For example, whilst Ni is the most active 3d TM catalyst for conventional DRM at 900 °C, NiFe alloy was found to be the best catalyst for CL-DRM.^[196]

The concept of exposing the redox catalyst (i.e. oxygen carriers) to two alternating atmospheres is also analogous to the “step-wise” approach used to study direct CO₂-CH₄ coupling reactions.^[165,197,198] Therefore, we anticipate future research in chemical looping systems to enable breakthroughs in traditionally challenging CO₂ conversion reactions, including those involving C-C coupling.

The physical circulation of oxygen carriers between the two reactors also enables effective heat management cf. stationary reactors, which rely primarily on thermal conduction.^[199] The reaction heat involved in each sub-reactor could be further tuned through oxygen carrier formulation. For example, Yusuf *et al.* demonstrated the possibility of tuning the endothermicity in each chemical looping reactor by varying the Fe-Mn ratio of a Na₂WO₄ promoted Fe-Mn-O mixed oxide redox catalyst.^[200] Of course, the overall endothermicity of the CO₂-driven hydrocarbon oxidation processes is ultimately determined by reaction stoichiometry. Present-day industry practice is to provide reaction heat by process fluids or fuel-firing, in order to maintain the desired operating temperature at the expense of increased CO₂ emission

and potentially reduced product selectivity (due to steep temperature gradients across the reactor). To fully exploit the carbon abatement potential of the CO₂ reduction processes, renewables should be used to supply the reaction heat, ideally in the most efficient way possible.

4.3. Renewable energy heating

The need for external heating by dry reforming and other CO₂-driven oxidation reactions is ubiquitous. In the context of CCU, the use of renewable energy heating, in the form of solar thermal heating or resistive heating by renewable electricity, could further increase the CO₂ abatement potential of the processes discussed above. Indeed, the concepts of solar membrane reactor,^[177,201] solar chemical looping reactor,^[202–206] and solar fixed-bed reactor^[207–209] have been adopted by many as the basis for achieving zero-emission dehydrogenation reactions^[210] and syngas production.^[207,208] Owing to the high endothermicity, solar thermal dry reforming is also regarded as a form of solar energy storage, in which CO₂ acts as a thermochemical storage medium.^[211–213] In a typical solar thermal reformer, the solar receiver is integrated with the thermal chemical reaction chamber to maximize heat transfer efficiency; one such example is schematically shown in Figure 10 (e).^[214] The same reactor designs could be adapted for solar-thermal CO₂-ODH and CO₂-OCM.^[215,216]

Compared to direct solar-thermal heating, which requires sophisticated optical and heat management equipment (Figure 10 e), resistively heating using renewable electricity is a plausible alternative to achieve truly carbon negative chemical production. In the chemical industry, replacing fuel-heated or steam-heated reactors with electrical heated ones has already attracted considerable R&D interests.^[217] An adequately engineered renewable-electricity-heated reactor can achieve not only net-zero-emission, but also a significantly optimized temperature profile within the reactor, rendering high effectiveness. The analysis by Wismann *et al.* showed that electrifying the reactor wall can potentially reduce the size of methane reformers by a factor of 100, owing to improved temperature uniformity and consequently more efficient catalyst utilization, as depicted in Figure 10 (f).^[218] Meanwhile, a major obstacle to the electrification of chemical reactors is the high energy cost of electricity compared to fuel fuels. Rissman *et al.* estimated that an electrically heated system needs to be 3 times more efficient than the fuel-heated equivalent in order for process plant electrification to be commercially viable.^[219]

5. Challenges and Opportunities

5.1. Status of development

The hydrogen-free reductive CO₂ conversion processes discussed in this review cover the production of a wide range of bulk chemicals. These processes also span a wide spectrum of technological readiness levels (TRLs). Therefore, the needs for research focus also differs significantly depending on the status of development of individual technologies, as shown in Table 1. From Table 1, it is apparent that all of the CO₂ utilization processes reviewed are many pilot-scale demonstrations away from commercial deployment, whilst catalyst development remains the most important aspect of research in the near future.

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Amongst these processes, the dry reforming of bio-derived feedstocks is the most technologically mature. By conducting experimental and computational investigations in carefully designed environments, researchers have established profound understanding of the structural-functional relationships for DRM catalysts, and have developed catalysts with outstanding performance accordingly. Current challenges limiting the advancement of the DRM technology include the complete elimination of carbon formation and developing effective methods to manage the strong endothermicity. The catalytic dry reforming of other biomass-derived feedstocks (viz. bio-ethanol, bio-glycerol and bio-oil) suffer more severely from carbon deposition than DRM and require periodic catalyst regeneration (e.g. by steam oxidation) to maintain long-term operational stability. The need for regeneration, which reduces overall process efficiency, can be substantially reduced by designing catalysts that do not coke. Moving forward, we anticipate the scientific understanding of coking during DRM to facilitate and accelerate the development of coke-resistant catalysts for DRE, DRG and DRB applications.

Table 1. Summary of estimated TRLs of the H₂-free CO₂ reduction and the key research required for making technological breakthroughs. The TRLs are estimated following the EU definition.^[220]

Reaction type	TRL	Research breakthrough required
Dry reforming	4 - 6	<ul style="list-style-type: none"> Eliminate carbon formation Reactor heat management
CO ₂ -ODH	4	<ul style="list-style-type: none"> Improve alkane conversion whilst maintaining high selectivity Mitigating carbon deposition Efficient product separation
OCM	3 - 4	<ul style="list-style-type: none"> Improve catalyst formulation to enhance methane conversion and C₂ yield
CO ₂ -epoxidation	4	<ul style="list-style-type: none"> Mitigate carbon deposition Suppress unselective C-C dissociation
Cyclic carbonation	9	<ul style="list-style-type: none"> Avoid the use of co-catalyst Develop heterogeneous catalysts
Direct CH ₄ -CO ₂ coupling	1 - 3	<ul style="list-style-type: none"> Identify reactor configurations for improved product yield

For CO₂-ODH, the desired structures of the active sites, viz. bifunctional oxide interfaces consisting of mild acidity and high redox activity, have been identified. Based on this understanding, researchers have developed catalysts showing high alkene yields (>60% in the case of CO₂-ODHEB) and near 100% alkene selectivities. In contrast, significantly fewer studies have been devoted to addressing the issue of catalyst deactivation due to coking. Furthermore, the separation and purification of the complex product mixtures would give rise to high parasitic energy penalties, which could be reduced by novel reactor concepts described in section 4.

Reduction reactions involving C-C coupling (e.g. CO₂-OCM, and CO₂-CH₄ coupling) require highly specific active sites, often located at oxide-oxide interfaces. Computational methods, such as DFT calculations, have been shown effective in identifying and evaluating such interfacial active sites. Moving forward, substantial research effort is required to develop catalyst formulations providing sufficiently high concentration of C-C coupling sites, whilst eliminating the presence of any unselective

active sites, e.g. those catalyzing C-C cleavage. In the case of direct CO₂-CH₄ coupling, much exploratory work is needed to identify the optimal reactor configurations which will give practically meaningful product yields.

5.2. Potential for CO₂ reduction

Several life cycle assessments have been performed on reductive CO₂ conversion using green hydrogen.^[3,4,6,18] These studies indicate that techno-commercial feasibility is limited by the high cost of green hydrogen, and the unreasonably high electricity demand. While the bulk chemical manufacturing processes described in this review do not consume hydrogen, most of these processes still occur exothermically at high temperatures (>500 °C). Only a life cycle assessment explicitly considering planetary boundary conditions can address the relative impact of chemical synthesis using expensive green hydrogen and excess electricity, versus chemical synthesis using hydrogen-free processes with higher thermal duties. In the following, we estimate the total CO₂ abatement potential of the renewable H₂-free CO₂ reduction processes discussed in this review.

Table 2. Estimated CO₂ abatement potential and renewable H₂ avoidance by the synthesizing selected bulk chemicals using captured CO₂ as a feedstock under the best case scenario.

Product	Reaction	GWP abatement (t-CO ₂ /t-product)	Total CO ₂ abatement (Mt-CO ₂)	Renewable H ₂ avoided (Mt)
Bio-syngas	DRM	2.0	9	0.0
Bio-syngas	DRE	2.0	213	0.0
Bio-syngas	DRG	2.0	8	0.0
Ethane	CO ₂ -OCM	1.6	240	10.7
Ethylene	CO ₂ -ODHE	1.6	240	10.7
Propylene	CO ₂ -ODHP	1.0	109	5.2
Styrene	CO ₂ -ODHEB	0.4	15	0.7
Butadiene	CO ₂ -ODHB	1.6	27	0.6
Ethylene oxide	CO ₂ -EE	2.8	93	0.8
Propylene oxide	CO ₂ -EP	2.8	29	0.2
Total	-	-	984	28.9

In Table 2, we show that the total reduction in cradle-to-gate CO₂ emissions for each product and the alleviated demands for renewable H₂. The reduction in H₂ demand is calculated by determining the hydrogen requirements to reduce an equivalent amount of CO₂ through RWGS. We assume the ideal scenario of 100% selectivity towards the desired products and that the reaction heat is supplied by renewables. The scale of bio-syngas production from CO₂ is estimated based on the global availability of bio-methane, bio-ethanol and bio-glycerol, whereas the production scales of other CO₂-derived bulk chemicals (e.g. alkenes and epoxides) are estimated based on current market demand. Using the data in 2017, the H₂-free CO₂ reduction processes covered in this review have an estimated combined

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abatement potential of 0.98 Gtpa-CO₂, which corresponds to (i) an 8.4 times increase in CO₂ utilization rate compared to current practices, (ii) 35% of the total industrial CO₂ emission and (iii) 2.7% of the total anthropogenic CO₂ emission.^[3,221] Crucially, since none of these processes require green hydrogen as inputs, these H₂-free CO₂ reduction processes can potentially reduce renewable H₂ demand by at least 28.9 Mtpa, which is equivalent to renewable energy savings of 1.24 PWh, or 3.78% of the world's total energy consumption by 2030, assuming DOE's 2020 target efficiency of centralized water electrolysis of 43 kWh/kg H₂.^[6,222]

6. Conclusions

In this review, we focus on the challenges and opportunities in synthesizing high-volume bulk chemicals (methanol, olefins, epoxides) from captured CO₂ without direct hydrogen input. These synthesis routes produce two marketable streams; namely the hydrocarbon products and CO. We discuss how dry reforming, dehydrogenation, oxidative coupling, and epoxidation can generate these bulk chemicals from captured CO₂, biogas, biomass, recycled waste, and shale gas. These reactions are generally catalyzed by metal nanoparticles on oxide supports having Lewis acid, base, and redox sites. Such multi-functional active site architectures are required to enable hydrocarbon activation (C-H and C-O) on the acid sites, C-C dissociation on the metal atoms, and O-CO dissociation on the base/redox sites. Tuning the acid site strength has a significant impact on reaction selectivity. Moderately acidic sites selectively activate C-H bonds while strong acid sites catalyze unselective cracking and deep-dehydrogenation which engenders coke formation. Designing catalysts with high selectivity and coking resistance remain two enduring challenges for these CO₂ utilization reactions. While coking has been mitigated for dry reforming catalysts by using molten catalysts^[98] or oxy-carbides^[99], comparatively limited progress has been made in designing coke-resistant catalysts for the other high temperature reactions discussed. There is also a knowledge gap in performing high-throughput screening of the multi-functional catalysts. The field is however at a stage where our foundational knowledge acquired through multi-modal spectroscopic characterization^[223] of the multicomponent oxides, and our understanding from increasingly accurate first principles computational modeling^[224,225] can be translated into robust design principles. These design principles which describe acid, base, and redox functions using simple physico-chemical descriptors can accelerate the hypothesis-based design of stable, selective, and active multi-functional catalysts for the aforementioned high temperature applications.

The CO₂ utilization reactions reviewed here also have limitations on conversions imposed by thermodynamics. Such limitations can be circumvented through reaction engineering approaches, such as membrane reactors and chemical looping reactors. Both reactor concepts could also significantly reduce the cost of product separation by inherently avoiding mixing of the reactants. In addition, membrane reactors and chemical looping systems decouple the redox cycle, thus enabling the design of more selective catalysts for CO₂ reduction and hydrocarbon oxidation, respectively. The decoupling of the redox cycle also provides more flexibility in selecting favorable reaction conditions to mitigate problems such as carbon deposition. The requirements for catalyst formulations in membrane reactors and chemical

looping are markedly different from conventional packed bed reactors used for lab scale catalytic testing. Therefore, more catalyst evaluation studies should be performed in these new reactor configurations. To minimize the overall CO₂ footprint, it is also preferable to meet the energy requirements of the endothermic reactions using renewable energy. Some approaches that have been successfully integrated with chemical reactions include solar thermal heating, and resistive heating using renewable electricity.

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References

- [1] Shell, *Shell Energy Transition Report*, **2017**.
- [2] M. D. Burkart, N. Hazari, C. L. Tway, E. L. Zeitler, *ACS Catal.* **2019**, *9*, 7937–7956.
- [3] A. Otto, T. Grube, S. Schiebahn, D. Stolten, *Energy Environ. Sci.* **2015**, *8*, 3283–3297.
- [4] R. G. Grim, Z. Huang, M. T. Guarnieri, J. R. Ferrell, L. Tao, J. A. Schaidle, *Energy Environ. Sci.* **2020**, *13*, 472–494.
- [5] C. Hepburn, E. Adlen, J. Beddington, E. A. Carter, S. Fuss, N. Mac Dowell, J. C. Minx, P. Smith, C. K. Williams, *Nature* **2019**, *575*, 87–97.
- [6] A. Kätelhön, R. Meys, S. Deutz, S. Suh, A. Bardow, *PNAS* **2019**, *116*, 11187–11194.
- [7] A. W. Kleij, M. North, A. Urakawa, *ChemSusChem* **2017**, *10*, 1036–1038.
- [8] M. North, R. Pasquale, C. Young, *Green Chem.* **2010**, *12*, 1514–1539.
- [9] M. Bowker, *ChemCatChem* **2019**, *11*, 4238–4246.
- [10] S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, T. F. Jaramillo, I. Chorkendorff, *Chem. Rev.* **2019**, *119*, 7610–7672.
- [11] Z. Wang, H. Song, H. Liu, J. Ye, *Angew. Chem. Int. Ed.* **2020**, *59*, 8016–8035.
- [12] S. Liu, L. R. Winter, J. G. Chen, *ACS Catal.* **2020**, *10*, 2855–2871.
- [13] C. Vogt, M. Monai, G. J. Kramer, B. M. Weckhuysen, *Nat. Catal.* **2019**, *2*, 188–197.
- [14] H. T. Luk, C. Mondelli, D. C. Ferré, J. A. Stewart, J. Pérez-Ramírez, *Chem. Soc. Rev.* **2017**, *46*, 1358–1426.
- [15] E. Gomez, B. Yan, S. Kattel, J. G. Chen, *Nat Rev Chem* **2019**, *3*, 638–649.
- [16] S. Schemme, J. L. Breuer, R. C. Samsun, R. Peters, D. Stolten, *J CO₂ Util.* **2018**, *27*, 223–237.
- [17] V. Zainzinger, *Chemical & Engineering News* **2020**, 98.

REVIEW

- [18] A. González-Garay, M. S. Frei, A. Al-Qahtani, C. Mondelli, G. Guillén-Gosálbez, J. Pérez-Ramírez, *Energy Environ. Sci.* **2019**, *12*, 3425–3436.
- [19] B. M. Tackett, E. Gomez, J. G. Chen, *Nat. Catal.* **2019**, *2*, 381.
- [20] J. Mertens, R. Belmans, M. Webber, *C—Journal of Carbon Research* **2020**, *6*, 39.
- [21] International Energy Agency, DECHEMA, ICCA, *Technology Road Map. Energy and GHG Reductions in the Chemical Industry via Catalytic Processes*, IEA Publications, Paris, **2013**.
- [22] X. Xiaoding, J. A. Moulijn, *Energ. Fuel* **1996**, *10*, 305–325.
- [23] J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* **2018**, *118*, 434–504.
- [24] V. R. Choudhary, K. C. Mondal, *Appl. Energy* **2006**, *83*, 1024–1032.
- [25] S. Kawi, Y. Kathiraser, *Front. Energy Res.* **2015**, *3*, DOI 10.3389/fenrg.2015.00013.
- [26] D. Pakhare, J. Spivey, *Chem. Soc. Rev.* **2014**, *43*, 7813–7837.
- [27] S. Koonaphapdeelert, P. Aggarangsi, J. Moran, *Biomethane: Production and Applications*, Springer Singapore, **2020**.
- [28] RFA, *2017 Ethanol Industry Outlook*, Renewable Fuels Association, **2017**.
- [29] H. Balat, E. Kirtay, *Int. J. Hydrog. Energy* **2010**, *35*, 7416–7426.
- [30] W. Wang, Y. Wang, *Int. J. Hydrog. Energy* **2009**, *34*, 5382–5389.
- [31] L. V. Mattos, G. Jacobs, B. H. Davis, F. B. Noronha, *Chem. Rev.* **2012**, *112*, 4094–4123.
- [32] J. R. Hannon, L. R. Lynd, O. Andrade, P. T. Benavides, G. T. Beckham, M. J. Biddy, N. Brown, M. F. Chagas, B. H. Davison, T. Foust, T. L. Junqueira, M. S. Laser, Z. Li, T. Richard, L. Tao, G. A. Tuskan, M. Wang, J. Woods, C. E. Wyman, *PNAS* **2019**, DOI 10.1073/pnas.1821684116.
- [33] X. Wang, M. Li, M. Wang, H. Wang, S. Li, S. Wang, X. Ma, *Fuel* **2009**, *88*, 2148–2153.
- [34] M. Suresh, C. P. Jawahar, A. Richard, *Renew. Sust. Energ. Rev.* **2018**, *92*, 38–49.
- [35] M. R. Monteiro, C. L. Kugelmeier, R. S. Pinheiro, M. O. Batalha, A. da Silva César, *Renew. Sust. Energ. Rev.* **2018**, *88*, 109–122.
- [36] M. Anitha, S. K. Kamarudin, N. T. Kofli, *Chem. Eng. J.* **2016**, *295*, 119–130.
- [37] V. K. Garlapati, U. Shankar, A. Budhiraja, *Biotechnol. Rep.* **2016**, *9*, 9–14.
- [38] N. N. Mohd Arif, S. Z. Abidin, O. U. Osazuwa, D.-V. N. Vo, M. T. Azizan, Y. H. Taufiq-Yap, *Int. J. Hydrog. Energy* **2019**, *44*, 20857–20871.
- [39] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, *Green Chemistry* **2008**, *10*, 13–30.
- [40] D. Wang, S. Czernik, E. Chornet, *Energ. Fuel* **1998**, *12*, 19–24.
- [41] S. Authayanun, D. Saebea, Y. Patcharavorachot, S. Assabumrungrat, A. Arpornwicheanop, *Int. J. Hydrog. Energy* **2017**, *42*, 1977–1988.
- [42] H. Xie, Q. Yu, H. Lu, Y. Zhang, J. Zhang, Q. Qin, *Int. J. Hydrog. Energy* **2017**, *42*, 28718–28731.
- [43] G.-Q. Yang, H. Wang, T. Gong, Y.-H. Song, H. Feng, H.-Q. Ge, H. Ge, Z.-T. Liu, Z.-W. Liu, *J. Catal.* **2019**, *380*, 195–203.
- [44] Mordor Intelligence, *Butadiene Market - Growth, Trends, and Forecast (2020 - 2025)*, Research And Markets, **2020**.
- [45] J. H. Lunsford, *Angew. Chem. Int. Ed. in English* **1995**, *34*, 970–980.
- [46] A. H. TULLO, *Chem. Eng. News Archive* **2011**, *89*, 20–21.
- [47] T. Nishiyama, K.-I. Aika, *J. Catal.* **1990**, *122*, 346–351.
- [48] J. W. Harris, L. Wang, J. F. DeWilde, *Ind. Eng. Chem. Res.* **2019**, *58*, 19061–19071.
- [49] P. D. Mobley, J. E. Peters, N. Akunuri, J. Hlebak, V. Gupta, Q. Zheng, S. J. Zhou, M. Lail, *Energy Procedia* **2017**, *114*, 7154–7161.
- [50] K. Wittich, M. Krämer, N. Bottke, S. A. Schunk, *ChemCatChem* **2020**, *12*, 2130–2147.
- [51] S. M. Kim, P. M. Abdala, T. Margossian, D. Hosseini, L. Foppa, A. Armutlulu, W. van Beek, A. Comas-Vives, C. Copéret, C. Müller, *J. Am. Chem. Soc.* **2017**, *139*, 1937–1949.
- [52] L. Foppa, M.-C. Silaghi, K. Larmier, A. Comas-Vives, *J. Catal.* **2016**, *343*, 196–207.
- [53] F. Qu, Y. Wei, W. Cai, H. Yu, Y. Li, S. Zhang, C. Li, *Energ. Fuel* **2018**, *32*, 2104–2116.
- [54] A. Drif, N. Bion, R. Brahm, S. Ojala, L. Pirault-Roy, E. Turpeinen, P. K. Seelam, R. L. Keiski, F. Epron, *Appl. Catal. A-Gen.* **2015**, *504*, 576–584.
- [55] A. M. da Silva, K. R. de Souza, G. Jacobs, U. M. Graham, B. H. Davis, L. V. Mattos, F. B. Noronha, *Appl. Catal. B.* **2011**, *102*, 94–109.
- [56] M. Tavanarad, F. Meshkani, M. Rezaei, *Catal Lett* **2018**, *148*, 164–172.
- [57] S. Bac, Z. Say, Y. Kocak, K. E. Ercan, M. Harfouche, E. Ozensoy, A. K. Avci, *Appl. Catal. B.* **2019**, *256*, 117808.
- [58] P. S. Bulutoglu, Z. Say, S. Bac, E. Ozensoy, A. K. Avci, *Appl. Catal. A-Gen.* **2018**, *564*, 157–171.
- [59] J. Huang, Y. Yan, S. Saqline, W. Liu, B. Liu, *Appl. Catal. B.* **2020**, *275*, 119109.
- [60] M. Akri, S. Zhao, X. Li, K. Zang, A. F. Lee, M. A. Isaacs, W. Xi, Y. Gangarajula, J. Luo, Y. Ren, Y.-T. Cui, L. Li, Y. Su, X. Pan, W. Wen, Y. Pan, K. Wilson, L. Li, B. Qiao, H. Ishii, Y.-F. Liao, A. Wang, X. Wang, T. Zhang, *Nat. Comm.* **2019**, *10*, 5181.
- [61] Y. Tang, Y. Wei, Z. Wang, S. Zhang, Y. Li, L. Nguyen, Y. Li, Y. Zhou, W. Shen, F. F. Tao, P. Hu, *J. Am. Chem. Soc.* **2019**, *141*, 7283–7293.
- [62] E. Ruckenstein, Y. H. Hu, *Appl. Catal. A-Gen.* **1995**, *133*, 149–161.
- [63] Y. H. Hu, E. Ruckenstein, *Science* **2020**, *368*, DOI 10.1126/science.abb5459.
- [64] K. Tomishige, O. Yamazaki, Y. Chen, K. Yokoyama, X. Li, K. Fujimoto, *Catal. Today* **1998**, *45*, 35–39.
- [65] B.-Q. Xu, J.-M. Wei, H.-Y. Wang, K.-Q. Sun, Q.-M. Zhu, *Catal. Today* **2001**, *68*, 217–225.
- [66] J. Feng, Y. Ding, Y. Guo, X. Li, W. Li, *Fuel* **2013**, *109*, 110–115.
- [67] Y. Song, E. Ozdemir, S. Ramesh, A. Adishev, S. Subramanian, A. Harale, M. Albuali, B. A. Fadhel, A. Jamal, D. Moon, S. H. Choi, C. T. Yavuz, *Science* **2020**, *367*, 777–781.
- [68] M. B. Bahari, N. H. H. Phuc, B. Abdullah, F. Alenazey, D.-V. N. Vo, *Renew. Energy J. Environ. Chem. Eng.* **2016**, *4*, 4830–4838.
- [69] M. B. Bahari, N. H. H. Phuc, F. Alenazey, K. B. Vu, N. Ainirazali, D.-V. N. Vo, *Catal. Today* **2017**, *291*, 67–75.
- [70] F. Fayaz, L. G. Bach, M. B. Bahari, T. D. Nguyen, K. B. Vu, R. Kanthasamy, C. Samart, C. Nguyen-Huy, D.-V. N. Vo, *Int. J. Energy Res.* **2019**, *43*, 405–416.
- [71] D. Cao, W. Cai, Y. Li, C. Li, H. Yu, S. Zhang, F. Qu, *Catal Lett* **2017**, *147*, 2929–2939.
- [72] D. Cao, F. Zeng, Z. Zhao, W. Cai, Y. Li, H. Yu, S. Zhang, F. Qu, *Fuel* **2018**, *219*, 406–416.
- [73] M. Tavanarad, F. Meshkani, M. Rezaei, *J CO2. Util.* **2018**, *24*, 298–305.
- [74] N. N. M. Arif, N. Harun, N. M. Yunus, D.-V. N. Vo, M. T. Azizan, S. Z. Abidin, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* **2017**, *39*, 657–663.
- [75] H. C. Lee, K. W. Siew, J. Gimbut, C. K. Cheng, *Chem. Eng. J.* **2014**, *255*, 245–256.
- [76] N. N. M. Arif, D.-V. N. Vo, M. T. Azizan, S. Z. Abidin, *Bull. Chem. React. Eng. Catal.* **2016**, *11*, 200–209.
- [77] K. W. Siew, H. C. Lee, J. Gimbut, C. K. Cheng, *Int. J. Hydrog. Energy* **2014**, *39*, 6927–6936.

REVIEW

- [78] K. W. Siew, H. C. Lee, J. Gimbut, S. Y. Chin, M. R. Khan, Y. H. Taufiq-Yap, C. K. Cheng, *Renewable Energy* **2015**, *74*, 441–447.
- [79] K. W. Siew, H. C. Lee, M. R. Khan, J. Gimbut, C. K. Cheng, *J. Energy Chem.* **2015**, *24*, 366–373.
- [80] N. Harun, J. Gimbut, M. T. Azizan, S. Z. Abidin, *Bull. Chem. React. Eng. Catal.* **2016**, *11*, 220–229.
- [81] N. Harun, S. Z. Abidin, O. U. Osazuwa, Y. H. Taufiq-Yap, M. T. Azizan, *Int. J. Hydrog. Energy* **2019**, *44*, 213–225.
- [82] X. Yao, Q. Yu, G. Xu, Z. Han, H. Xie, W. Duan, Q. Qin, *Int. J. Hydrog. Energy* **2018**, *43*, 22108–22115.
- [83] H. Xie, R. Li, Z. Yu, Z. Wang, Q. Yu, Q. Qin, *Energy* **2020**, *200*, 117481.
- [84] T. Hou, L. Yuan, T. Ye, L. Gong, J. Tu, M. Yamamoto, Y. Torimoto, Q. Li, *Int. J. Hydrog. Energy* **2009**, *34*, 9095–9107.
- [85] D. Wang, D. Montané, E. Chornet, *Appl. Catal. A-Gen.* **1996**, *143*, 245–270.
- [86] L. Garcia, R. French, S. Czernik, E. Chornet, *Appl. Catal. A-Gen.* **2000**, *201*, 225–239.
- [87] M. Fu, W. Qi, Q. Xu, S. Zhang, Y. Yan, *Int. J. Hydrog. Energy* **2016**, *41*, 1494–1501.
- [88] X. Qingli, F. Peng, Q. Wei, H. Kai, X. Shanzhi, Y. Yongjie, *Int. J. Hydrog. Energy* **2019**, *44*, 10277–10285.
- [89] G. R. Moradi, M. Rahmanzadeh, F. Khosravian, *J. CO₂ Util.* **2014**, *6*, 7–11.
- [90] M.-S. Fan, A. Z. Abdullah, S. Bhatia, *ChemCatChem* **2009**, *1*, 192–208.
- [91] A. A. S. Oliveira, R. L. B. A. Medeiros, G. P. Figueredo, H. P. Macedo, R. M. Braga, F. V. Maziviero, M. A. F. Melo, D. M. A. Melo, M. M. Vieira, *Int. J. Hydrog. Energy* **2018**, *43*, 9696–9704.
- [92] N. Bonmassar, M. F. Bekheet, L. Schlicker, A. Gili, A. Gurlo, A. Doran, Y. Gao, M. Heggen, J. Bernardi, B. Klötzer, S. Penner, *ACS Catal.* **2020**, *10*, 1102–1112.
- [93] E. P. Komarala, I. Komissarov, B. A. Rosen, *Catalysts* **2020**, *10*, 27.
- [94] S. Dama, S. R. Ghodke, R. Bobade, H. R. Gurav, S. Chilukuri, *Appl. Catal. B.* **2018**, *224*, 146–158.
- [95] I. Rivas, J. Alvarez, E. Pietri, M. J. Pérez-Zurita, M. R. Goldwasser, *Catal. Today* **2010**, *149*, 388–393.
- [96] N. Wang, X. Yu, Y. Wang, W. Chu, M. Liu, *Catal. Today* **2013**, *212*, 98–107.
- [97] R. C. Rabelo-Neto, H. B. E. Sales, C. V. M. Inocência, E. Varga, A. Oszko, A. Erdohelyi, F. B. Noronha, L. V. Mattos, *Appl. Catal. B.* **2018**, *221*, 349–361.
- [98] C. Palmer, D. C. Upham, S. Smart, M. J. Gordon, H. Metiu, E. W. McFarland, *Nat. Catal.* **2020**, *3*, 83–89.
- [99] R. Thakur, A. VahidMohammadi, J. Smith, M. Hoffman, J. Moncada, M. Beidaghi, C. A. Carrero, *ACS Catal.* **2020**, *10*, 5124–5134.
- [100] D. Mukherjee, S.-E. Park, B. M. Reddy, *J. CO₂ Util.* **2016**, *16*, 301–312.
- [101] M. B. Ansari, S.-E. Park, *Energy Environ. Sci.* **2012**, *5*, 9419–9437.
- [102] Y. He, Z. Yang, Z. Liu, P. Wang, M. Guo, J. Ran, *ChemistrySelect* **2020**, *5*, 2232–2239.
- [103] X.-L. Xue, W.-Z. Lang, X. Yan, Y.-J. Guo, *ACS Appl. Mater. Interfaces* **2017**, *9*, 15408–15423.
- [104] V. D. B. C. Dasireddy, M. Huš, B. Likozar, *Catal. Sci. Technol.* **2017**, *7*, 3291–3302.
- [105] B. M. Reddy, H. Jin, D.-S. Han, S.-E. Park, *Catal. Lett.* **2008**, *124*, 357–363.
- [106] K. Ren, J. Song, Y.-H. Song, H. Wang, Z. Liu, Z.-T. Liu, J. Jiang, Z.-W. Liu, *J. CO₂ Util.* **2017**, *22*, 63–70.
- [107] R. Koirala, R. Buechel, S. E. Pratsinis, A. Baiker, *Appl. Catal. A-Gen.* **2016**, *527*, 96–108.
- [108] I. Kainthla, G. V. R. Babu, J. T. Bhanushali, K. S. R. Rao, B. M. Nagaraja, *J. CO₂ Util.* **2017**, *18*, 309–317.
- [109] N. Mimura, M. Okamoto, H. Yamashita, S. T. Oyama, K. Murata, *J. Phys. Chem. B* **2006**, *110*, 21764–21770.
- [110] L. Jin, J. Reutenauer, N. Opembe, M. Lai, D. J. Martenak, S. Han, S. L. Suib, *ChemCatChem* **2009**, *1*, 421–421.
- [111] B. P. Ajayi, B. Rabindran Jermy, B. A. Abussaud, S. Al-Khattaf, *J. Porous Mater.* **2013**, *20*, 1257–1270.
- [112] G. Raju, B. M. Reddy, B. Abhishek, Y.-H. Mo, S.-E. Park, *Appl. Catal. A-Gen.* **2012**, *423–424*, 168–175.
- [113] G. Raju, B. M. Reddy, S.-E. Park, *J. CO₂ Util.* **2014**, *5*, 41–46.
- [114] P. Michorczyk, K. Zeńczak-Tomera, B. Michorczyk, A. Węgrzyniak, M. Basta, Y. Millot, L. Valentin, S. Dzwigaj, *J. CO₂ Util.* **2020**, *36*, 54–63.
- [115] T. A. Bugrova, V. V. Dutov, V. A. Svetlichnyi, V. Cortés Corberán, G. V. Mamontov, *Catal. Today* **2019**, *333*, 71–80.
- [116] X. Li, S. Liu, H. Chen, S. Luo, F. Jing, W. Chu, *ACS Omega* **2019**, *4*, 22562–22573.
- [117] Z. Xie, Y. Ren, J. Li, Z. Zhao, X. Fan, B. Liu, W. Song, L. Kong, X. Xiao, J. Liu, G. Jiang, *J. Catal.* **2019**, *372*, 206–216.
- [118] X. Ye, Y. Yue, C. Miao, Z. Xie, W. Hua, Z. Gao, *Green Chem.* **2005**, *7*, 524–528.
- [119] Z.-W. Liu, C. Wang, W.-B. Fan, Z.-T. Liu, Q.-Q. Hao, X. Long, J. Lu, J.-G. Wang, Z.-F. Qin, D. S. Su, *ChemSusChem* **2011**, *4*, 341–345.
- [120] B. Xu, B. Zheng, W. Hua, Y. Yue, Z. Gao, *J. Catal.* **2006**, *239*, 470–477.
- [121] B. Zheng, W. Hua, Y. Yue, Z. Gao, *J. Catal.* **2005**, *232*, 143–151.
- [122] H. Xiao, J. Zhang, P. Wang, X. Wang, F. Pang, Z. Zhang, Y. Tan, *Catal. Sci. Technol.* **2016**, *6*, 5183–5195.
- [123] R. Koirala, R. Buechel, F. Krumeich, S. E. Pratsinis, A. Baiker, *ACS Catal.* **2015**, *5*, 690–702.
- [124] M. Chen, J.-L. Wu, Y.-M. Liu, Y. Cao, L. Guo, H.-Y. He, K.-N. Fan, *Appl. Catal. A-Gen.* **2011**, *407*, 20–28.
- [125] M. Chen, J. Xu, Y.-M. Liu, Y. Cao, H.-Y. He, J.-H. Zhuang, *Appl. Catal. A-Gen.* **2010**, *377*, 35–41.
- [126] D. R. Burri, K.-M. Choi, D.-S. Han, Sujandi, N. Jiang, A. Burri, S.-E. Park, *Catal. Today* **2008**, *131*, 173–178.
- [127] A. Burri, N. Jiang, K. Yahyaoui, S.-E. Park, *Appl. Catal. A-Gen.* **2015**, *495*, 192–199.
- [128] L. Zhang, Z. Wu, N. C. Nelson, A. D. Sadow, I. I. Slowing, S. H. Overbury, *ACS Catal.* **2015**, *5*, 6426–6435.
- [129] H.-X. Fan, J. Feng, W.-Y. Li, X.-H. Li, T. Wiltowski, Q.-F. Ge, *Appl. Surf. Sci.* **2018**, *427*, 973–980.
- [130] H. Wang, G.-Q. Yang, Y.-H. Song, Z.-T. Liu, Z.-W. Liu, *Catal. Today* **2019**, *324*, 39–48.
- [131] T. Wang, X. Guan, H. Lu, Z. Liu, M. Ji, *Appl. Surf. Sci.* **2017**, *398*, 1–8.
- [132] P. Ch., R. K. V. v., V. R. M., N. P., S. R. R. K., D. R. B., *J. Ind. Eng. Chem.* **2019**, *79*, 97–105.
- [133] A. Tóth, G. Halasi, F. Solymosi, *J. Catal.* **2015**, *330*, 1–5.
- [134] A. Tóth, G. Halasi, T. Bánsági, F. Solymosi, *J. Catal.* **2016**, *337*, 57–64.
- [135] R. Jin, J. Easa, D. T. Tran, C. P. O'Brien, *Catal. Sci. Technol.* **2020**, *10*, 1769–1777.
- [136] E. Nowicka, C. Reece, S. M. Althahban, K. M. H. Mohammed, S. A. Kondrat, D. J. Morgan, Q. He, D. J. Willock, S. Golunski, C. J. Kiely, G. J. Hutchings, *ACS Catal.* **2018**, *8*, 3454–3468.
- [137] M. Myint, B. Yan, J. Wan, S. Zhao, J. G. Chen, *J. Catal.* **2016**, *343*, 168–177.
- [138] B. Yan, S. Yao, J. G. Chen, *ChemCatChem* **2020**, *12*, 494–503.
- [139] E. Gomez, S. Kattel, B. Yan, S. Yao, P. Liu, J. G. Chen, *Nat. Comm.* **2018**, *9*, 1398.
- [140] X. Li, B. Yan, S. Yao, S. Kattel, J. G. Chen, T. Wang, *Appl. Catal. B.* **2018**, *231*, 213–223.
- [141] T. Wang, S. Chong, T. Wang, H. Lu, M. Ji, *Appl. Surf. Sci.* **2018**, *427*, 1011–1018.
- [142] L. Wang, Y. Wang, R. Zhang, R. Ding, X. Chen, B. Lv, *ACS Catal.* **2020**, *6697–6706*.
- [143] G. Siddiqi, P. Sun, V. Galvita, A. T. Bell, *J. Catal.* **2010**, *274*, 200–206.
- [144] Y. Wang, Y. Takahashi, Y. Ohtsuka, *J. Catal.* **1999**, *186*, 160–168.

REVIEW

- [145] Y. Wang, Y. Takahashi, Y. Ohtsuka, *Chem. Lett.* **1998**, 27, 1209–1210.
- [146] Y. Wang, Y. Ohtsuka, *J. Catal.* **2000**, 192, 252–255.
- [147] Y. Wang, Y. Ohtsuka, *Appl. Catal. A-Gen.* **2001**, 219, 183–193.
- [148] Y. Cai, L. Chou, S. Li, B. Zhang, J. Zhao, *Catal. Lett.* **2003**, 86, 191–195.
- [149] I. Istadi, N. A. Saidina Amin, *J. Nat. Gas Chem.* **2004**, 13, 23–25.
- [150] Y. Zhang, Y. Cho, A. Yamaguchi, X. Peng, M. Miyauchi, H. Abe, T. Fujita, *Sci. Rep.* **2019**, 9, 15454.
- [151] F. D. Monica, A. W. Kleij, *Catal. Sci. Technol.* **2020**, 10, 3483–3501.
- [152] T. Aida, S. Inoue, *J. Am. Chem. Soc.* **1983**, 105, 1304–1309.
- [153] X.-B. Lu, W.-M. Ren, G.-P. Wu, *Acc. Chem. Res.* **2012**, 45, 1721–1735.
- [154] D.-A. Yang, H.-Y. Cho, J. Kim, S.-T. Yang, W.-S. Ahn, *Energy Environ. Sci.* **2012**, 5, 6465–6473.
- [155] Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu, K. Ding, *Angew. Chem. Int. Ed.* **2007**, 46, 7255–7258.
- [156] T. Zhang, X. Wang, X. Huang, Y. Liao, J. Chen, *RSC Adv.* **2016**, 6, 2810–2818.
- [157] R. Srivastava, D. Srinivas, P. Ratnasamy, *Catal. Lett.* **2003**, 89, 81–85.
- [158] P. Puthiaraj, S. Ravi, K. Yu, W.-S. Ahn, *Appl. Catal. B.* **2019**, 251, 195–205.
- [159] N. Mulchandani, V. Katiyar, in *Advances in Sustainable Polymers: Synthesis, Fabrication and Characterization* (Eds.: V. Katiyar, A. Kumar, N. Mulchandani), Springer, Singapore, **2020**, pp. 35–49.
- [160] L. J. Farrugia, S. Lopinski, P. A. Lovatt, R. D. Peacock, *Inorg. Chem.* **2001**, 40, 558–559.
- [161] E. Hori, in *Modern Aspects of Electrochemistry 42* (Eds.: C.G. Vayenas, R.E. White, M.E. Gamboa-Aldeco), Springer-Verlag, New York, **2008**, pp. 89–189.
- [162] J. Na, B. Seo, J. Kim, C. W. Lee, H. Lee, Y. J. Hwang, B. K. Min, D. K. Lee, H.-S. Oh, U. Lee, *Nat. Comm.* **2019**, 10, 5193.
- [163] Y. Fujiwara, Y. Taniguchi, K. Takaki, M. Kurioka, T. Jintoku, T. Kitamura, *Stud. Surf. Sci. Catal.* **1997**, 107, 275–278.
- [164] A. T. Bell, S. Gaemers, S. Mukhopadhyay, M. J. Muskett, J. G. Sunley, M. Zerella, *Process for Production of Acetyl Anhydrides and Optionally Acetic Acid from Methane and Carbon Dioxide*, **2005**, WO2005009927A3.
- [165] S. Wang, S. Guo, Y. Luo, Z. Qin, Y. Chen, M. Dong, J. Li, W. Fan, J. Wang, *Catal. Sci. Technol.* **2019**, 9, 6613–6626.
- [166] R. Shavi, J. Ko, A. Cho, J. W. Han, J. G. Seo, *Appl. Catal. B.* **2018**, 229, 237–248.
- [167] Y. Zhao, C. Cui, J. Han, H. Wang, X. Zhu, Q. Ge, *J. Am. Chem. Soc.* **2016**, 138, 10191–10198.
- [168] Y. Zhao, H. Wang, J. Han, X. Zhu, D. Mei, Q. Ge, *ACS Catal.* **2019**, 9, 3187–3197.
- [169] Y. Zhao, H. Wang, J. Han, X. Zhu, Q. Ge, *J. Phys. Chem. C* **2018**, 122, 9570–9577.
- [170] J. Coronas, M. Menendez, J. Santamaria, *Ind. Eng. Chem. Res.* **1995**, 34, 4229–4234.
- [171] B. K. Abdalla, S. S. E. H. Elnashaie, *J. Membr. Sci.* **1993**, 85, 229–239.
- [172] S. Dangwal, R. Liu, S.-J. Kim, *Chem. Eng. J.* **2017**, 328, 862–872.
- [173] W. Yang, H. Wang, X. Zhu, L. Lin, *Top Catal.* **2005**, 35, 155–167.
- [174] S. Pati, J. Ashok, N. Dewangan, T. Chen, S. Kawi, *J. Membr. Sci.* **2020**, 595, 117496.
- [175] H. Jiang, Z. Cao, S. Schirmermeister, T. Schiestel, J. Caro, *Angew. Chem. Int. Ed.* **2010**, 49, 5656–5660.
- [176] G. Dimitrakopoulos, R. C. Schucker, K. Derrickson, J. R. Johnson, K. K. Kopeć, L. Shao, F. Alahmadi, A. F. Ghoniem, *ECS Trans.* **2017**, 80, 181.
- [177] R. Michalsky, D. Neuhaus, A. Steinfeld, *Energy Technol.* **2015**, 3, 784–789.
- [178] W. Wang, Y. S. Lin, *J. Membr. Sci.* **1995**, 103, 219–233.
- [179] P. Zhang, J. Tong, K. Huang, *ACS Sustain. Chem. Eng.* **2019**, DOI 10.1021/acssuschemeng.8b06430.
- [180] S.-W. Choi, D. S. Sholl, S. Nair, J. S. Moore, Y. Liu, R. S. Dixit, J. G. Pendergast, *AIChE J.* **2017**, 63, 4519–4531.
- [181] C. J. Dittrich, *Chem. Eng. J.* **2020**, 381, 122492.
- [182] A. Brune, T. Wolff, A. Seidel-Morgenstern, C. Hamel, *Chemie Ingenieur Technik* **2019**, 91, 645–650.
- [183] L. M. Neal, S. Yusuf, J. A. Sofranko, F. Li, *Energy Technol.* **n.d.**, 4, 1200–1208.
- [184] S. Chen, L. Zeng, R. Mu, C. Xiong, Z.-J. Zhao, C. Zhao, C. Pei, L. Peng, J. Luo, L.-S. Fan, J. Gong, *J. Am. Chem. Soc.* **2019**, 141, 18653–18657.
- [185] V. Fleischer, P. Littlewood, S. Parishan, R. Schomäcker, *Chem. Eng. J.* **2016**, 306, 646–654.
- [186] S. Parishan, P. Littlewood, A. Arinchtin, V. Fleischer, R. Schomäcker, *Catal. Today* **2018**, 311, 40–47.
- [187] V. Fleischer, U. Simon, S. Parishan, M. G. Colmenares, O. Görke, A. Gurlo, W. Riedel, L. Thum, J. Schmidt, T. Risse, K.-P. Dinse, R. Schomäcker, *J. Catal.* **2018**, 360, 102–117.
- [188] Z. Cheng, D. S. Baser, S. G. Nadgouda, L. Qin, J. A. Fan, L.-S. Fan, *ACS Energy Lett.* **2018**, 3, 1730–1736.
- [189] M. S. C. Chan, E. Marek, S. A. Scott, J. S. Dennis, *J. Catal.* **2018**, 359, 1–7.
- [190] E. J. Marek, S. Gabra, J. S. Dennis, S. A. Scott, *Appl. Catal. B.* **2020**, 262, 118216.
- [191] H. Wang, X. Dong, T. Zhao, H. Yu, M. Li, *Appl. Catal. B.* **2019**, 245, 302–313.
- [192] G. Wei, J. Huang, Y. Fan, Z. Huang, A. Zheng, F. He, J. Meng, D. Zhang, K. Zhao, Z. Zhao, H. Li, *Energy. Conv. Manag.* **2019**, 179, 304–313.
- [193] D. Hosseini, P. M. Abdala, F. Donat, S. M. Kim, C. R. Müller, *Appl. Catal. B.* **2019**, 258, 117946.
- [194] J. Guerrero-Caballero, T. Kane, N. Haidar, L. Jalowiecki-Duhamel, A. Löfberg, *Catal. Today* **2019**, 333, 251–258.
- [195] L. Yu, W. Zhou, Z. Luo, H. Wang, W. Liu, K. Yin, *Adv. Sustain. Syst.* **n.d.**, n/a, 2000099.
- [196] J. Huang, W. Liu, Y. Yang, B. Liu, *ACS Catal.* **2018**, 1748–1756.
- [197] W. Huang, K.-C. Xie, J.-P. Wang, Z.-H. Gao, L.-H. Yin, Q.-M. Zhu, *J. Catal.* **2001**, 201, 100–104.
- [198] Y. Liu, N. Cui, P. Jia, W. Huang, *Catalysts* **2020**, 10, 131.
- [199] X. Zhu, F. Donat, Q. Imtiaz, C. R. Müller, F. Li, *Energy Environ. Sci.* **2020**, DOI 10.1039/C9EE03793D.
- [200] S. Yusuf, V. Haribal, D. Jackson, L. Neal, F. Li, *Appl. Catal. B.* **2019**, 257, 117885.
- [201] H. Wang, M. Liu, H. Kong, Y. Hao, *Appl. Therm. Eng.* **2019**, 152, 925–936.
- [202] J. R. Fosheim, B. J. Hathaway, J. H. Davidson, *Energy* **2019**, 169, 597–612.
- [203] K. J. Warren, R. J. Carrillo, B. Greek, C. M. Hill, J. R. Scheffe, *Energy Technol.* **2020**, n/a, 2000053.
- [204] S. Chuayboon, S. Abanades, S. Rodat, *J. Energy Chem.* **2020**, 41, 60–72.
- [205] Y. Liu, Q. Zhu, T. Zhang, X. Yan, R. Duan, *Renew. Energy* **2020**, 154, 863–874.
- [206] X. Liu, H. Zhang, H. Hong, H. Jin, *Appl. Energy* **2020**, 268, 114995.
- [207] S. A. M. Said, M. Waseeuddin, D. S. A. Simakov, *Renew. Sustain. Energy Rev.* **2016**, 59, 149–159.
- [208] A. Tavasoli, G. Ozin, *Joule* **2018**, 2, 571–575.
- [209] H. Zhang, Y. Shuai, B. G. Lougou, B. Jiang, F. Wang, Z. Cheng, H. Tan, *Appl. Energy* **2020**, 265, 114799.
- [210] F. Lei, L. Freiberg, Y. Wang, I. Reddick, G. Jovanovic, A. Yokochi, N. AuYeung, *Chem. Eng. J.* **2019**, 355, 58–64.
- [211] T. Yu, Q. Yuan, J. Lu, J. Ding, Y. Lu, *Appl. Energy* **2017**, 185, 1994–2004.
- [212] X. Chen, F. Wang, Y. Han, R. Yu, Z. Cheng, *Energy. Conv. Manag.* **2018**, 158, 489–498.
- [213] C. Chen, M. Kong, S. Zhou, A. E. Sepulveda, H. Hong, *Appl. Energy* **2020**, 266, 114788.

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- [214] A. Berman, R. K. Karn, M. Epstein, *Green Chem.* **2007**, *9*, 626–631.
- [215] C. Agrafiotis, H. von Storch, M. Roeb, C. Sattler, *Renew. Sust. Energ. Rev.* **2014**, *29*, 656–682.
- [216] C. Agrafiotis, M. Roeb, C. Sattler, *Renew. Sust. Energ. Rev.* **2015**, *42*, 254–285.
- [217] Brightlands, “Petrochemical companies form Cracker of the Future Consortium and sign R&D agreement,” can be found under <https://www.brightlands.com/brightlands-smart-services-campus/actueel-nieuws-en-evenementen>, **2019**.
- [218] S. T. Wismann, J. S. Engbæk, S. B. Vendelbo, F. B. Bendixen, W. L. Eriksen, K. Aasberg-Petersen, C. Frandsen, I. Chorkendorff, P. M. Mortensen, *Science* **2019**, *364*, 756–759.
- [219] J. Rissman, C. Bataille, E. Masanet, N. Aden, W. R. Morrow, N. Zhou, N. Elliott, R. Dell, N. Heeren, B. Huckestein, J. Cresko, S. A. Miller, J. Roy, P. Fennell, B. Cremmins, T. Koch Blank, D. Hone, E. D. Williams, S. de la Rue du Can, B. Sisson, M. Williams, J. Katzenberger, D. Burtraw, G. Sethi, H. Ping, D. Danielson, H. Lu, T. Lorber, J. Dinkel, J. Helseth, *Appl. Energy* **2020**, *266*, 114848.
- [220] European Commission Decision C, *European Commission Decision C(2017)2468 of 24 April 2017*, **2017**.
- [221] H. Ritchie, M. Roser, *Our World in Data* **2017**.
- [222] Department of Energy, “DOE Technical Targets for Hydrogen Production from Electrolysis,” can be found under <https://www.energy.gov/eere/fuelcells/doe-technical-targets-hydrogen-production-electrolysis>, **n.d.**
- [223] P. Hemberger, J. A. van Bokhoven, J. Pérez-Ramírez, A. Bodi, *Catalysis Science & Technology* **2020**, *10*, 1975–1990.
- [224] M. Capdevila-Cortada, Z. Łodziana, N. López, *ACS Catal.* **2016**, *6*, 8370–8379.
- [225] R. Rousseau, V.-A. Glezakou, A. Selloni, *Nat. Rev. Mater.* **2020**, *5*, 460–475.

Entry for the Table of Contents

This review discusses the advances so far, and the future research required for the large-scale deployment of reductive CO₂ utilization processes that circumvent the requirement for renewable hydrogen. By developing high performance catalysts and highly efficient reactor systems, we envisage a potential to reduce the CO₂ footprint of the chemical industry by 1 Gtpa, whilst avoiding the need for 29 Mtpa of renewable H₂.

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